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NONLINEAR OPTICAL EFFECTS IN CRYSTALS

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INTRODUCTION

THE application of optical quantum generators (lasers) to study condensed systems (crystals or liquids) has made it possible to observe an entire set of non-linear optical effects.^[1-7] We can explain them in essence as follows.

For example, let us assume that a condensed system is being subjected to the action of two intense fluxes of electromagnetic radiation of frequencies ω_1 and ω_2 . Then fluxes appear in this system with frequencies $2\omega_1$, $2\omega_2$, and $\omega_1 \pm \omega_2$. That is, sum, difference, and double frequencies are produced. If the system shows absorption in even one of the spectral regions $2\omega_1$, $2\omega_2$, or $\omega_1 \pm \omega_2$, one can then observe a so-called two-photon absorption. That is, two photons disappear and some state of the condensed system, having an energy equal to the sum of the energies of the photon, is excited. The processes cited above are termed non-linear. More than two elementary excitations (photons, phonons, etc.) participate in these processes. In a number of cases, they become appreciable only when the primary fluxes have high enough intensities. It is interesting to note that this type of phenomenon has been known for a relatively long time in the microwave and radio regions. This involves the fact that it was specifically in the microwave and radio regions that the high-power fluxes necessary for observation of non-linear effects could first be obtained. Only very recently have people been able to obtain high-power fluxes in the optical region of the spectrum as well. In this review we shall limit ourselves mainly to discussing third-order non-linear effects for the optical range.

We note that some non-linear effects can occur

even at low intensities of incident radiation fluxes. Thus, the long-known Raman scattering in crystals is essentially a non-linear process; it is the result of the interaction of an electromagnetic wave with the lattice vibrations. Finally, ordinary absorption, which can be considered as the transformation of the energy of electromagnetic waves into lattice vibrations, is also a non-linear process in a certain sense.

In interacting with fluxes of electromagnetic radiation, a crystal acts as a transformer of electromagnetic-radiation energy, as S. I. Vavilov^[8] has pointed out. We shall consider here in fuller detail some stages of this transformation that will be of great interest to us later on.

Let electromagnetic radiation characterized by the frequencies ω_1 and ω_2 be incident on the crystal. When the electromagnetic radiation passes through the crystal-vacuum boundary, the characteristic normal vibrations arise in the crystal with their characteristic frequencies.

These vibrations are oscillations of the electrons and nuclei of the crystal associated with the oscillations of the electromagnetic field. Strictly speaking, one cannot distinguish mechanical oscillations of particles from electromagnetic oscillations. Such a situation is sometimes referred to as the "mixing" of states of excitons and transverse photons. Owing to the "mixing", observable optical waves are formed, i.e., normal characteristic vibrations or real excitons (excitons with retardation taken into account).^[9-15]

We can consider these characteristic vibrations to be independent only in the zero-order approximation; taking anharmonicity into account entails that the vibrations exchange energy. A state of the

crystal characterized by intense enough vibrations of frequencies ω_1 and ω_2 has a probability of going over to states of frequencies $2\omega_1$, $2\omega_2$, or $\omega_1 + \omega_2$. The latter in turn generate electromagnetic waves of the stated frequencies, and the detector records the presence of the double, sum, and difference frequencies.

Let us consider the phenomenon of Raman scattering in an analogous way. For concreteness, we limit ourselves at first to the Stokes component. The incident light flux excites in the crystal a normal vibration of frequency ω_0 , which is transformed into two vibrations of frequencies ω_1 and ω_2 , where $\omega_0 = \omega_1 + \omega_2$. The vibration of frequency ω_1 induces electromagnetic waves, which are recorded as the Stokes component of the Raman spectrum, while the vibration of frequency ω_2 (a phonon) is subsequently transformed into heat. The anti-Stokes component is to be treated analogously: vibrations of frequencies ω_0 and ω_2 combine and form a vibration of frequency $\omega_0 + \omega_2$. The latter induces an electromagnetic wave, which is recorded as the anti-Stokes component of the Raman spectrum.

The first study on the theory of non-linear optical processes in crystals was apparently one by I. E. Tamm^[16] concerned with the theory of Raman scattering. In this study he considered Raman scattering as the result of interaction of the normal vibrations in the crystal. However, Tamm's study was semi-phenomenological in nature, since he did not calculate the anharmonicity coefficients explicitly. Furthermore, a knowledge of these coefficients is necessary for determination of the fundamental characteristics of Raman scattering. The concrete calculation of the anharmonicity coefficients mentioned in^[16] has proved possible within the framework of the relatively recent microtheory.^[11] According to this theory, the Hamiltonian of the system (electrons, nuclei, and radiation field) can be expanded in powers of the amplitudes of the crystal vibrations. A treatment of the Hamiltonian to an accuracy of the second order in the amplitudes permits one to obtain the energy spectrum of the normal vibrations in the crystal.^[11] Taking account of the remainder of the Hamiltonian gives rise to the non-linear processes.^[18-20]

Ordinary crystal optics takes another approach to the problem of determining the spectrum of the normal vibrations of the crystal. As we know (see, e.g.^[17,13]), a knowledge of the dielectric-constant tensor $\epsilon_{ij}(\omega, \mathbf{k})$ permits us to determine the refractive indices, i.e., to find the relation of the frequency of a normal vibration to its wave vector. This relation is found from the formula $(\omega^2/c^2)n^2 = k^2$, where ω is the frequency, c is the velocity of light in vacuo, n is the refractive index, and \mathbf{k} is the wave vector. In recent years, people have paid attention to the fact that it is essential to take into

account the phenomenon of spatial dispersion^[13,14] in a number of spectral regions. As we know, spatial dispersion leads to the appearance of certain new effects (optical activity, anisotropy of cubic crystals, new waves, etc.)

At present there are several variants of the theory of non-linear optical effects in crystals. In this regard, we shall mention first the extensive theoretical work of Bloembergen and his associates.^[30] In this study they investigated the action of an electromagnetic wave of frequency ω on the quantum-mechanical system. They found the perturbed wave function of the system, and then the dipole moment \mathbf{P} of the system in the perturbed state as a function of the electric-field intensity \mathbf{E} of the wave. The value of the dipole moment was represented as a series expansion

$$P_i = b_{ij}E_j + \beta_{ijk}E_jE_k + \dots, \quad (1)$$

where b_{ij} and β_{ijk} are certain characteristics of the system. If we are not considering a resonance region, the small parameter of this expansion is the ratio E/E_0 , where E_0 is the intramolecular field intensity, $E_0 \sim 10^7$ V/cm. Since the electric-field intensity E does not exceed $\sim 10^5$ V/cm, even in lasers, the ratio E/E_0 is small, and amounts to something of the order of 10^{-2} . We note that in the vicinity of a resonance, a large parameter $(\omega/\nu)f$ can generally accompany the small parameter E/E_0 . Here ν is the width of the resonance line and f is the oscillator strength. If, e.g., $\omega \sim 10^{15}$ sec⁻¹, $\nu \sim 10^{12}$ sec⁻¹, and $f \sim 0.1$, then $(\omega/\nu)f \sim 10^2$, and the problem of the convergence of the series (1) requires special treatment. If we limit ourselves in the expansion (1) to only the linear approximation, i.e., assume $\beta = 0$, etc., we arrive at the ordinary linear theory. In this framework, the non-linear effects are absent. However, if we take into account the higher terms in the expansion of \mathbf{P} in powers of \mathbf{E} (i.e., assume that $\beta \neq 0 \dots$), then non-linear effects become possible. By using (1) and Maxwell's equations, one can show (see^[30]) that under the action of a field of frequency ω , the dipole moment per unit volume also contain higher harmonics. They arise from the presence in (1) of terms containing the higher powers of the field \mathbf{E} . Hence, waves of frequencies 2ω , 3ω , etc., appear in the medium.

This very sort of consideration has been used in^[28-32,60-69] (see also the review^[71]). Loudon has used a somewhat different approach.^[57]

Here the radiation field was quantized, and the non-linear optical effects arise from the interaction between the crystal and the radiation, which is considered as a weak perturbation. This approach seems more consistent to us, since one can consider within this framework such a problem, e.g., as the radiation width. However, the mentioned difficulties in the vicinity of resonances persist even here.

We shall mention also ^[72], which took into account the effect of quadrupole transitions on non-linear effects. These transitions become important in crystals having inversion centers, in which third-order non-linear effects are forbidden in the dipole approximation. Study ^[73] took up the interaction of radiation with free electrons, which also leads to the appearance of sum harmonics.

Reference ^[74] was concerned with calculating the coherent interaction length of radiation in a non-linear medium, while ^[75] discussed the problem of the passage of random signals through a non-linear medium. The problem of the existence of fluctuations in non-linear effects due to a spread in the phases and amplitudes of the different modes has been taken up in ^[76].

The studies ^[28-32,60-69,57,72-76] cited above give a qualitatively true description of non-linear optical effects in dielectrics. However, their results are limited in applicability to small oscillator strengths of the transitions in the crystal, and to a frequency region far enough removed from absorption bands (for more details, see Sec. 7). All these limitations are eliminated naturally if we use as the unperturbed states those states corresponding to the excitation in the crystal of real light waves in the medium (excitons with retardation taken into account) (see ^[11,18,19]). It was shown in these studies that a theory of non-linear optical effects can be developed on the basis of the method used in ^[11]. This method (see ^[18,19]) permits one strictly to isolate the third-order anharmonic terms as well as the quadratic terms in the Hamiltonian (properly speaking, in ^[11] the treatment was limited specifically to the quadratic terms).

The specific isolation of the third-order terms corresponding to scattering of light waves by phonons was first made in ^[18]. This made it possible to study the long-wavelength edge of an absorption band. In contrast to ^[18], a theory was developed in ^[19,20] permitting one to study from a unified viewpoint the interaction of the normal vibrations of any type, and to describe such phenomena as frequency doubling, the effect of sum-harmonic generation, the phenomenon of two-photon absorption, and the corresponding luminescence. This approach permits one to construct a microtheory of Raman scattering in crystals, and to give an explanation of the peculiarities of scattering in piezoelectrics. It is free from the difficulties found in the earlier theories when non-linear effects were studied in the vicinity of a resonance.

A feature of ^[18-20] on which the treatment below is based is the fact that it was not assumed therein that the interaction between the radiation field and the crystal is weak. This fact proves to be essential, since in a number of spectral regions the interaction between the radiation field and the crystal is actually not weak. Taking account of this fact leads to a num-

ber of observable effects, which cannot be treated within the framework of the perturbation theory in terms of the interaction cited above (see Sec. 7). All of the problems mentioned above will be elucidated in more detail below. The first chapter will present the general theory of non-linear effects, while the following text will discuss a number of concrete effects on the basis of this theory.

I. THE GENERAL THEORY OF NON-LINEAR EFFECTS

1. The expression for the Hamiltonian

As we stated above, we must isolate the anharmonicity terms in studying non-linear effects in the complete Hamiltonian of the system including electrons, nuclei, and the radiation field. If here the Hamiltonian is limited merely to taking into account the terms that are quadratic in the vibration amplitudes of the crystal, then the corresponding expression can be exactly diagonalized. It is essential to note that the normal vibrations thus arising are nothing other than electromagnetic waves in the medium obeying Maxwell's equations.^[21] Hence, in discussing the anharmonicity terms below within the framework of the perturbation theory, we thereby assume that electromagnetic waves in the medium satisfying Maxwell's linear equations are a good zero-order approximation of the theory.

In connection with what has been said, in this chapter the terms will be isolated that are essential in describing non-linear effects.

Everywhere below we shall limit ourselves to discussing the optical properties of a crystal in those spectral regions that do not involve the excitation of free current carriers in the crystal. Consequently, we shall essentially limit ourselves to studying non-linear optical effects in the region of the exciton absorption bands.

At first we shall limit ourselves to discussing a molecular crystal having fixed molecules. This means that the centers of gravity and directions of the principal axes of inertia of the molecules are fixed, although intramolecular vibrations can occur in the molecule. We shall indicate below what changes arise in the theory if we reject these limitations.

If we use the Coulomb gauge of the electromagnetic radiation field,^[22] then we can write the Hamiltonian of the system in the form

$$H = H_1 + H_2 + H_3, \quad (1.1)$$

where H_1 is the Hamiltonian of the crystal taking into account only the instantaneous Coulombic interaction between the charges, H_2 is the Hamiltonian of the field of transverse photons, and H_3 is the interaction between the field of these photons and the charges.

In this approximation, following ^[11], we shall write

the Hamiltonian of the crystal in the form

$$H_1 = \sum_{f,s} E_f b_{f,s}^\dagger b_{f,s} + \frac{1}{2} \sum_{\substack{s \neq s_1 \\ f, s; f', s; f, s_1; f', s_1}} V_{s, s_1}(f, s; f', s; f, s_1; f', s_1) b_{f,s}^\dagger b_{f',s}^\dagger b_{f',s} b_{f,s}, \quad (1.2)$$

where s is the number of the unit cell of the crystal, f is the set of indices specifying the number of the molecule in the unit cell and the number of the level in the molecule, E_f are the levels of the unperturbed molecule, $V(\dots)$ are the matrix elements of the intermolecular-interaction operator, and $b_{f,s}^\dagger, b_{f,s}$ are the so-called Pauli operators. These operators characterize the creation and annihilation of the f -th state in the s -th unit cell, and obey the commutation relations

$$b_i b_i^\dagger + b_i^\dagger b_i = 1, \\ b_i b_{i'}^\dagger - b_{i'}^\dagger b_i = 0, \quad i \neq i'$$

(i is an abbreviation for f, s).

The Hamiltonian of the transverse photons has the form [22]

$$H_2 = \sum_{\mathbf{q}, j} \hbar \omega_{\mathbf{q}, j} a_{\mathbf{q}, j}^\dagger a_{\mathbf{q}, j}, \quad (1.3)$$

where \mathbf{q} is the wave vector of the photon, j is the polarization number, and $a_{\mathbf{q}, j}^\dagger(\mathbf{q})$ and $a_{\mathbf{q}, j}(\mathbf{q})$ are operators for creation and annihilation of photons.

The interaction operator H_3 consists of two terms: [22]

$$H_3 = H_3^I + H_3^{II} = - \sum_{s,p} \frac{e_p}{m_p c} (\mathbf{I}_{s,p}, \mathbf{A}(\mathbf{r}_{s,p})) \\ + \sum_{s,p} \frac{e_p^2}{2m_p c} A^2(\mathbf{r}_{s,p}), \quad (1.4)$$

where p is an index giving the number of the molecule in the crystalline unit cell and the number of the particle (electron or nucleus) in the molecule, $e_p, m_p, \mathbf{I}_{s,p}$, and $\mathbf{r}_{s,p}$ are the charge, mass, momentum operator, and radius vector of the s -th particle in the p th unit cell, respectively, and $\mathbf{A}\{\mathbf{r}\}$ is the vector potential. We can write Eq. (1.4) in the second-quantization representation in terms of the operators a^\dagger, a , and b^\dagger, b . Omitting the details of calculation, which can be found in [19], we shall give the final expression:

$$\left. \begin{aligned} H_3^I &= - \sum_{\mathbf{q}, i, f, f', s} \frac{e_p}{m_p} \sqrt{\frac{2\pi\hbar}{V\omega_{\mathbf{q}}}} (l_j(\mathbf{q})(\mathbf{I}_{s,p})_{ff'}) \\ &\quad \times b_{f',s}^\dagger b_{f,s} [a_j(\mathbf{q}) e^{i(\mathbf{q}, \mathbf{r}(s,p))} + a_j^\dagger(\mathbf{q}) e^{-i(\mathbf{q}, \mathbf{r}(s,p))}], \\ H_3^{II} &= \frac{\pi\hbar}{V} \sum_{\mathbf{q}_1, i_1, \mathbf{q}_2, i_2} \frac{(l_{j_1}(\mathbf{q}_1), l_{j_2}(\mathbf{q}_2))}{\sqrt{\omega_1 \omega_2}} \\ &\quad \times \{ a_{j_1}(\mathbf{q}_1) a_{j_2}(\mathbf{q}_2) \varphi(\mathbf{q}_1 + \mathbf{q}_2) \\ &\quad + 2a_{j_1}^\dagger(\mathbf{q}_1) a_{j_2}(\mathbf{q}_2) \varphi(\mathbf{q}_2 - \mathbf{q}_1) \\ &\quad + a_{j_1}^\dagger(\mathbf{q}_1) a_{j_2}^\dagger(\mathbf{q}_2) \varphi(-\mathbf{q}_1 - \mathbf{q}_2) \}, \end{aligned} \right\} (1.5a)$$

where

$$\varphi(\mathbf{q}) = \sum_{f, f', s} \Psi_{ff'}(\mathbf{q}) b_{f',s}^\dagger b_{f,s}, \\ \Psi_{ff'}(\mathbf{q}) = \left\{ \sum_p \frac{e_p^2}{m_p} e^{i(\mathbf{q}, \mathbf{r}(p))} \right\}_{f, f'}$$

$l_i(\mathbf{q})$ is the unit vector determining the polarization of the photon, and V is the volume of the crystal; the radius vector $\mathbf{r}(p)$ determines the position of the p -th particle in the unit cell.

We shall assume everywhere in the treatment below that the overwhelming majority of the molecules are in the ground state, and only an insignificant fraction in the excited state. This circumstance permits us to apply the approximate second quantization method developed by N. N. Bogolyubov. [23] That is, we use the following operators instead of the Pauli operators discussed above:

$$B_{f,s} = b_{f,s}^\dagger b_{f,s}, \quad B_{f',s}^\dagger = b_{f',s}^\dagger b_{f',s} \quad (1.6)$$

(the index $f = 0$ implies the ground state). To an accuracy of the ratio of the number of molecules in the excited state to the number of molecules in the ground state, these operators are Bose operators, as has been shown in [11].

2. Separation of the second- and third-order terms in the initial Hamiltonian

Our further problem consists in isolating the terms of different orders in the operators $a_j(\mathbf{q}), B_{f,s}$ in the expression for the complete Hamiltonian. We shall carry out this procedure separately for each term of (1.1).

First we shall consider the operator H_1 (see (1, 2)). By transforming to the operators $B_{f,s}$ in the expression for H_1 , we derive the following expression:

$$H_1 = H_1^{(2)} + H_1^{(3)}, \quad (2.1)$$

where

$$H_1^{(2)} = \sum_{f,s} E_f B_{f,s}^\dagger B_{f,s} + \frac{1}{2} \sum_{s s_1, f f'} \{ V_{s, s_1}(0, f, f', 0) B_{f',s}^\dagger B_{f,s} \\ + V_{s, s_1}(f, 0, 0, f') B_{f,s}^\dagger B_{f',s_1}^\dagger + V_{s, s_1}(0, f, 0, f') B_{f',s}^\dagger B_{f',s_1}^\dagger \\ + V_{s, s_1}(f, 0, f', 0) B_{f,s}^\dagger B_{f',s_1} \} \quad (2.1a)$$

is the quadratic part, and

$$H_1^{(3)} = \frac{1}{2} \sum_{s s_1 \{f\}} \{ V_{s, s_1}(0, f, f', f'') B_{f',s}^\dagger B_{f',s_1}^\dagger B_{f',s_1} \\ + V_{s, s_1}(f, 0, f', f'') B_{f,s}^\dagger B_{f',s_1}^\dagger B_{f',s_1} \\ + V_{s, s_1}(f, f', 0, f'') B_{f,s}^\dagger B_{f',s}^\dagger B_{f',s_1} \\ + V_{s, s_1}(f, 0, f', f'') B_{f,s}^\dagger B_{f',s}^\dagger B_{f',s_1} \} \quad (2.1b)$$

are the third-order terms.

The operator (2.1a) can be diagonalized by the substitution

$$B_{j,s} = N^{-1/2} \sum_{\mu k} [B_{\mu}(\mathbf{k}) u_{f\mu}(k) e^{i(\mathbf{k}, \mathbf{r}(s))} + B_{\mu}^{\dagger}(\mathbf{k}) v_{f\mu}^*(k) e^{-i\mathbf{k}\mathbf{r}(s)}], \quad (2.2)$$

where N is the number of unit cells in the crystal, $\mathbf{r}(s)$ is the radius vector determining the position of the s -th unit cell, and $B_{\mu}(\mathbf{k})$ are the new Bose operators. The coefficients $u_{f\mu}$ and $v_{f\mu}$ are determined from the system of equations

$$\begin{aligned} (E_f - E) u_f + \sum_{f'} (\Gamma_{ff'}^{(1)} u_{f'} + \Gamma_{ff'}^{(2)} v_{f'}) &= 0, \\ (E_f + E) v_f + \sum_{f'} (\Gamma_{ff'}^{(2)*} v_{f'} + \Gamma_{ff'}^{(1)*} u_{f'}) &= 0, \end{aligned} \quad (2.3)$$

where

$$\begin{aligned} \Gamma_{ff'} &= \sum_s V_{0s}(f, 0, 0, f') e^{i(\mathbf{k}, \mathbf{r}(s))}, \\ \Gamma_{ff'} &= \sum_s V_{0s}(0, f, 0, f') e^{i(\mathbf{k}, \mathbf{r}(s))}. \end{aligned} \quad (2.4)$$

In solving the homogeneous system of equations (2.3), we must take into account the normalization condition, which has the form

$$\sum_f (|u_f|^2 - |v_f|^2) = 1. \quad (2.5)$$

After we apply the substitution (2.2), Eq. (2.1a) acquires the form

$$H_1^{(2)} = \sum_{\mu, h} E_{\mu}(\mathbf{k}) B_{\mu}^{\dagger}(\mathbf{k}) B_{\mu}(\mathbf{k}), \quad (2.6)$$

where $E_{\mu}(\mathbf{k})$ are the roots of the secular equation of system (2.3), which determine the Coulombic-exciton energy spectrum.

Analogously, we can isolate the second- and third-order terms from the operator H_3 . Omitting the details of calculation (see [11, 19]), we obtain

$$H_3 = H_3^{(2)} + H_3^{(3)}, \quad (2.7)$$

where

$$H_3^{(2)} = H_3^{I(2)} + H_3^{II(2)} \quad (2.7a)$$

are the quadratic terms, and

$$H_3^{(3)} = H_3^{I(3)} + H_3^{II(3)} \quad (2.7b)$$

are the third-order terms.

Here the following notation has been introduced:

$$\begin{aligned} H_3^{I(2)} &= \sum_{\mathbf{q}, j, \mu} \{T(\mathbf{q}, j, \mu) a_j(\mathbf{q}) B_{\mu}^{\dagger}(\mathbf{q}) + T(-\mathbf{q}, j, \mu) a_j^{\dagger}(\mathbf{q}) B_{\mu}^{\dagger}(-\mathbf{q}) \\ &+ T^*(-\mathbf{q}, j, \mu) a_j(\mathbf{q}) B_{\mu}(-\mathbf{q}) + T^*(\mathbf{q}, j, \mu) a_j^{\dagger}(\mathbf{q}) B_{\mu}(\mathbf{q})\}, \end{aligned} \quad (2.8)$$

$$\begin{aligned} H_3^{II(3)} &= \sum_{\mathbf{q}, j, \mu_1, \mu_2} [R(\mathbf{q}, j, k, \mu_1, \mu_2) a_j(\mathbf{q}) B_{\mu_1}(\mathbf{k}) B_{\mu_2}^{\dagger}(\mathbf{k} + \mathbf{q}) \\ &+ R(-\mathbf{q}, j, \mathbf{k}, \mu_1, \mu_2) a_j^{\dagger}(\mathbf{q}) B_{\mu_1}(\mathbf{k}) B_{\mu_2}^{\dagger}(\mathbf{k} - \mathbf{q})], \end{aligned} \quad (2.9)$$

$$T(\mathbf{q}, j, \mu) = \sqrt{\frac{2\pi\hbar N}{Vqc}} \langle 0 | j | \mathbf{q}, \mu \rangle,$$

$$\langle 0 | j | \mathbf{q}, \mu \rangle = \sum_f (I_j(\mathbf{q}) M_{0f}(\mathbf{q})) u_{f\mu}(\mathbf{q}),$$

$$M(\mathbf{q}) = \sum_p \frac{e_p}{m_p} \mathbf{I}_p e^{i(\mathbf{q}, \mathbf{r}(p))},$$

$$R(\mathbf{q}, j, \mathbf{k}, \mu_1, \mu_2) = \sqrt{\frac{2\pi\hbar}{Vqc}} \langle \mathbf{q}, \mu_1 | j | \mathbf{q} + \mathbf{k}, \mu_2 \rangle,$$

$$\langle \mathbf{q}, \mu_1 | j | \mathbf{q} + \mathbf{k}, \mu_2 \rangle$$

$$= \sum_{f_1, f_2} (I_j(\mathbf{k}) M_{f_1, f_2}(\mathbf{k})) u_{f_1, \mu_1}(\mathbf{q}) u_{f_2, \mu_2}^*(\mathbf{q} + \mathbf{k}).$$

The expression for $H_3^{II(2)}$ is derived from (1.5) by replacing $\varphi(\mathbf{q}_1 - \mathbf{q}_2)$ by $N \sum_p (e_p^2/m_p) \delta(\mathbf{q}_1, \mathbf{q}_2)$,

where $\delta(\mathbf{q}_1, \mathbf{q}_2)$ is the Kronecker delta ($\delta(\mathbf{q}, \mathbf{q}) = 1$, but $\delta(\mathbf{q}_1, \mathbf{q}_2) = 0$ when $\mathbf{q}_1 \neq \mathbf{q}_2$). The expression for $H_3^{II(3)}$ is also derived from (1.5) by replacing $\varphi(\mathbf{q})$ by

$$N^{1/2} \sum_{f, p} (e^{i(\mathbf{q}, \mathbf{r}(p))} - 1)_{0f} \frac{e_p}{m_p} u_{f\mu}^*(\mathbf{q}) B_{\mu}^{\dagger}(\mathbf{q})$$

+ its complex conjugate.

Equation (1.3) need not be transformed, since it is diagonal in the variables a^+ and a .

3. Separation of the non-linear effect operator

The set of second-order terms entering into the complete Hamiltonian of the system consisting of electrons, nuclei, and the radiation field, i.e., the sum

$$H^{(2)} = H_1^{(2)} + H_2 + H_3^{(2)}, \quad (3.1)$$

can be diagonalized by the substitution

$$\begin{aligned} a_j(\mathbf{q}) &= \sum_{\rho} [u_{j\rho}(\mathbf{q}) \xi_{\rho}(\mathbf{q}) + v_j^{\dagger}(-\mathbf{q}) \xi_{\rho}^{\dagger}(-\mathbf{q})], \\ B_{\mu}(\mathbf{q}) &= \sum_{\rho} [u_{\mu\rho}(\mathbf{q}) \xi_{\rho}(\mathbf{q}) + v_{\mu\rho}^{\dagger}(-\mathbf{q}) \xi_{\rho}^{\dagger}(-\mathbf{q})]. \end{aligned} \quad (3.2)$$

Here the new Bose operators ξ^+ and ξ are operators for creation and annihilation of excitons with retardation taken into account (real electromagnetic waves in the crystal), and the subscript ρ specifies the branch number. The coefficients u and v entering into (3.2) are determined by a certain system of homogeneous equations (see [11, 19]) that we shall not copy here because of their cumbersomeness.

Upon transforming to the operators ξ^+ and ξ , Eq. (3.1) acquires the form

$$H^{(2)} = \sum_{\rho, \mathbf{k}} E_{\rho}(\mathbf{k}) \xi_{\rho}^{\dagger}(\mathbf{k}) \xi_{\rho}(\mathbf{k}), \quad (3.3)$$

where $E_{\rho}(\mathbf{k})$ is a root of the secular equation of the above mentioned system of homogeneous equations, from which one determines the coefficients u and v taking part in (3.2). The set of values of $E_{\rho}(\mathbf{k})$ gives the energy spectrum of excitons having retardation taken into account; this spectrum for the simplest case is shown in Fig. 1.

The coefficients for the transformation to the new

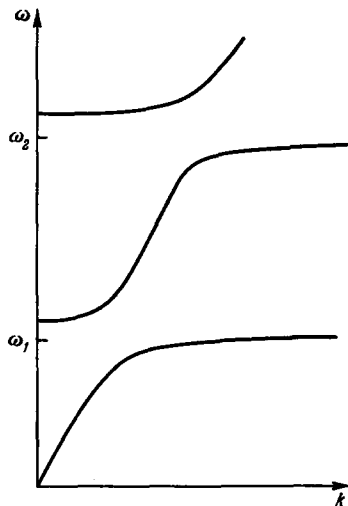


FIG. 1. Relation of the frequency of an exciton to the wave vector; the frequencies ω_1 , ω_2 , etc. correspond to the characteristic coulombic-exciton frequencies.

variables taking part in (3.2) have the following form:

$$\left. \begin{aligned} u_{j\rho} &= A^{-1}, \quad v_{j\rho} = \frac{\hbar qc - E_\rho(\mathbf{q})}{\hbar qc + E_\rho(\mathbf{q})} A^{-1}, \\ u_{\mu\rho} &= \frac{2\hbar qc T(\mathbf{q}j\mu)}{A[E_\mu(\mathbf{q}) - E_\rho(\mathbf{q})][\hbar qc + E_\rho(\mathbf{q})]}, \\ v_{\mu\rho} &= \frac{2\hbar qc T(\mathbf{q}j\mu)}{A[E_\mu(\mathbf{q}) + E_\rho(\mathbf{q})][\hbar qc + E_\rho(\mathbf{q})]}. \end{aligned} \right\} \quad (3.4)$$

Here the vector $l_i(\mathbf{q})$ lies in the direction of polarization of the ordinary or extraordinary ray in the crystal. The quantity A entering into (3.4) is determined from a normalization condition analogous to (2.5):

$$|u_j|^2 - |v_j|^2 + \sum_\mu \{|u_\mu(\mathbf{q})|^2 - |v_\mu(\mathbf{q})|^2\} = 1. \quad (3.5)$$

We must note that the quantity $E_\rho(\mathbf{k})$ is generally complex: its imaginary part characterizes the attenuation of the electromagnetic waves in the crystal.*

The third-order terms have the form

$$H^{(3)} = \sum_{\rho_1\rho_2\rho_3k_1k_2} Q_{\rho_1\rho_2\rho_3}(\mathbf{k}_1\mathbf{k}_2) \xi_{\rho_1}(\mathbf{k}_1) \xi_{\rho_2}(\mathbf{k}_2) \xi_{\rho_3}^+(\mathbf{k}_1 + \mathbf{k}_2) + \text{its complex conjugate}. \quad (3.6)$$

where $Q(\dots)$ are the coefficients obtained from all the third-order terms, i.e., those of Eqs. (2.7b) and

*We note in passing that the method presented above permits one to study the energy spectrum of a crystal occurring at a temperature of -0 . In [11], the crystal was studied at a temperature of $+0$, and it was assumed that almost all of the molecules were in the ground state. The assumption that the crystal is at a temperature -0 means that almost all the molecules are in the excited state. To find the exciton spectrum here we can use directly the results of [11]. However, one should substitute $-E_f$ for the energy E_f of the excited state of the molecule in all the formulas of that paper. The relation of the exciton energy to the wave vector for this case is shown schematically in Fig. 2.

(2.1b), upon transforming to the operators ξ . The terms of types $\xi^+\xi^+\xi^+$ and $\xi\xi\xi$ are omitted in writing (3.6), since they are not very important in the effects of interest to us. Eq. (3.6), considered as a perturbation with respect to the Hamiltonian of the zero-order approximation (3.3), directly describes the non-linear processes. It is important to emphasize that the procedure presented above permits one to obtain the cubic anharmonicity coefficients in explicit form. They are all expressed in terms of the characteristics of the individual molecules forming the crystal and the matrix elements of interaction between them. We shall not write out here the general form of these coefficients, which is rather cumbersome in the general case. It is more convenient to write it separately for each concrete case, as will be done below.

Let several exciton fluxes be propagated in the crystal. These can be characterized as a whole by some distribution of quantum numbers $n_\rho(\mathbf{k})$ characterizing the occupancy of the levels corresponding to the exciton states. As we have mentioned, these fluxes exchange energy owing to the non-linear interaction. Consequently some of them gain energy and others lose it. This exchange consists of a series of elementary events, each of which is: a) an event of formation of one exciton from the total energy of two (exciton combination), or b) an event of formation of two excitons from one (exciton decay). For a Hamiltonian taken with an accuracy to third-order terms in the creation and annihilation operators, there will be no other elementary events in the first approximation.

The rate of increase of the number of excitons through events of combination of other excitons is determined from the expression

$$\begin{aligned} \frac{dn}{dt}(\rho_3, \mathbf{k}_1 + \mathbf{k}_2) &= \frac{2\pi}{\hbar} \sum_{\rho_1\rho_2} |Q_{\rho_1\rho_2\rho_3}(\mathbf{k}_1, \mathbf{k}_2)|^2 n(\rho_1, \mathbf{k}_1) n(\rho_2, \mathbf{k}_2) \\ &\times [n(\rho_3, \mathbf{k}_1 + \mathbf{k}_2) + 1] \delta\{E_{\rho_1}(\mathbf{k}_1) + E_{\rho_2}(\mathbf{k}_2) - E_{\rho_3}(\mathbf{k}_1 + \mathbf{k}_2)\}. \end{aligned} \quad (3.7)$$

Analogously, the rate of increase of the number of excitons through decay events is determined by the

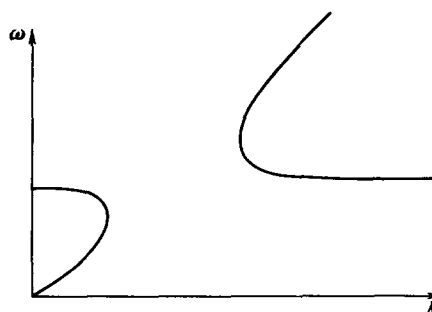


FIG. 2. Relation of the frequency of an exciton to the wave vector at a negative temperature.

expression

$$\begin{aligned} \frac{dn}{dt}(\rho_3, \mathbf{k}_1) = & \frac{2\pi}{\hbar} \sum_{\rho_1 \rho_2 \rho_3} |Q_{\rho_1 \rho_2 \rho_3}(\mathbf{k}_1, \mathbf{k}_2)|^2 n(\rho_3, \mathbf{k}_1 + \mathbf{k}_2) \\ & \times [n(\rho_1, \mathbf{k}_1) + 1][n(\rho_2, \mathbf{k}_2) + 1] \delta\{E_{\rho_1}(\mathbf{k}_1) + E_{\rho_2}(\mathbf{k}_2) \\ & - E_{\rho_3}(\mathbf{k}_1 + \mathbf{k}_2)\}. \end{aligned} \quad (3.8)$$

Generally, combination (or decay) events take place simultaneously with the reverse events of decay (or combination). For example, let us examine the process of generation of summed-energy excitons. If $n(\rho_3, \mathbf{k}_1 + \mathbf{k}_2) \ll 1$, then the "reverse" event of decay will be considerably less probable than the "direct" event of combination, according to Eqs. (3.7) and (3.8). Consequently, the process generating the Stokes component of the Raman spectrum at low intensity of the scattered flux can be directly calculated by Eq. (3.8), completely ignoring the "reverse" process. Arguing by analogy, we can conclude that the anti-Stokes component is found from Eq. (3.7). In exactly the same way, when the resultant fluxes are small, the process of generation of a sum frequency should be calculated by Eq. (3.7), and a difference frequency by Eq. (3.8). However, for large resultant intensities, i.e., when $n(\rho_3, \mathbf{k}_1 + \mathbf{k}_2) \ll 1$, the problem becomes more complex, and the direction that the process takes is determined by a number of other factors: the formula of the exciton branch, the spectral composition of the exciton fluxes, etc.

We can divide the non-linear effects into two groups: electronic and electronic-vibrational.

We shall refer to non-linear effects as electronic if they take place even when the vibrational motion in the crystal is completely neglected. Here we get a certain correction term (inessential as a rule) by taking the latter into account. These effects include: generation of sum and difference frequencies, two-photon excitation, and certain others. In order to obtain the third-order terms describing the electronic non-linear processes, we must take only the electronic states of the molecules as the f states.

We shall refer to the effects which result from the electronic-vibrational interaction as electronic-vibrational non-linear effects. These effects include: Raman scattering by intermolecular and intramolecular vibrations, and the generation of the Mandelstam-Brillouin component.

In order to obtain the third-order terms describing Raman scattering by the intramolecular vibrations, we must take as the f states both the electronic and the vibrational states of the molecule.

If we wish to study Raman scattering by the intermolecular vibrations or the Mandelstam-Brillouin components, we must relax the limitation made at the beginning of this section, and permit the molecules to move as a whole within the unit cell. Then the Hamiltonian of the crystal will contain coordinates charac-

terizing the optical intermolecular and acoustic vibrations of the crystal. Owing to the third-order terms involving the optical intermolecular vibrations, the Raman scattering will manifest these vibrations; owing to the third-order terms involving the acoustic vibrations, the Mandelstam-Brillouin components appear.

Now some words on the higher-order effects.

The operators B_f are only approximately Bose operators. Nevertheless, we need not take this fact into account in studying the Hamiltonian of the system to an accuracy of the third-order terms. However, we must do so if it becomes necessary to study the terms of higher than third order.

Various higher-order non-linear effects have been observed in a number of experimental studies: the appearance of third harmonics,^[25,26] and three-photon absorption.^[7] An attempt has been undertaken in^[27] to construct a theory of many-photon processes. However, this study does not take into account the circumstance pointed out above, and also has a number of defects that will be studied in detail in Sec. 7 of this review.

In concluding this section, we shall examine systematically the question that arises of the effect of the third-order terms on the elementary-excitation spectrum. Understandably, the role of the cubic terms increases with increasing flux intensity of quasiparticles in the crystal. Actually, such a phenomenon resembles the phenomenon of anharmonicity in the theory of ordinary mechanical vibrations: the more intense the vibrations are, the greater the role of anharmonicity.

We can estimate the correction to the energy by the standard formulas of the perturbation theory. Cubic anharmonicity contributes only in the second approximation of the perturbation theory. An estimate shows that the relative change of the exciton energy is

$$\frac{\Delta E}{E} \approx \gamma \frac{N_0}{N},$$

where N_0/N is the concentration of excitons in the crystal, and γ is a dimensionless coefficient considerably less than unity. Evidently, under real conditions, $\Delta E/E \ll 1$. One can draw an analogous conclusion upon taking fourth-order anharmonicity into account.

II. ELECTRONIC NONLINEAR EFFECTS

4. The generation of sum harmonics

In line with what we have said above, we shall call the effects for which the existence of electronic-vibrational interaction is not essential non-linear electronic effects. These effects include the phenomena of doubling and addition of frequencies, two-photon absorption, and certain others. This section

will discuss the generation of sum harmonics.

Let two intense monochromatic exciton fluxes be propagated in the crystal with frequencies ω_1 and ω_2 . The intensity of the resulting flux of frequency $\omega_1 + \omega_2$ is assumed to be small. This assumption imposes the following limitations on the quantum numbers $n(\rho, \mathbf{k})$ entering into Eqs. (3.7) and (3.8): the quantity $n(\rho_3, \mathbf{k}_1 + \mathbf{k}_2) \ll 1$, while $n(\rho_1, \mathbf{k}_1)$ is equal to some constant n_1 in a small region Γ_1 of \mathbf{k} -space and zero outside this region. The energy and wave vector of the excitons in Γ_1 are approximately equal to E_1 and \mathbf{k}_1 . The second flux has an analogous property, its corresponding characteristics being n_2 , Γ_2 , \mathbf{k}_2 , and E_2 .

Hence, in order to obtain the intensity of the sum harmonic, it suffices, upon setting $n(\rho_3, \mathbf{k}_1 + \mathbf{k}_2) = 0$ on the right-hand side of Eq. (3.7), to find

$$\frac{d}{dt} n(\rho_3) = \sum_{\mathbf{k}_1 \mathbf{k}_2} \frac{d}{dt} n(\rho_3, \mathbf{k}_1 + \mathbf{k}_2). \quad (4.1)$$

Owing to the presence of the δ function on the right-hand side of (3.7), the summation in Eq. (4.1) will cover a certain hypersurface in the space formed by the set $\mathbf{k}_1, \mathbf{k}_2$; the results of this summation depend on the structure of the exciton branches. It is expedient to transform from summation to integration over the energy E and the solid angle Ω . Here it is convenient to bring the factors that depend weakly on the variables of integration outside the integrand, as is usually done. Consequently, we find that

$$\frac{d}{dt} n(\rho_3) = \frac{2\pi}{\hbar} |Q_{\rho_1, \rho_2, \rho_3}(\mathbf{k}_1, \mathbf{k}_2)|^2 N_1 N_2 [\Delta E_1 \Delta E_2 \Delta \Omega_1 \Delta \Omega_2]^{-1} \times \int_{\tau} dE d\Omega_1 d\Omega_2, \quad (4.2)$$

where $N_1 = n_1 \rho(E_1) \Delta E_1 \Delta \Omega_1$ is the number of excitons in the crystal belonging to the flux of frequency ω_1 , and $\rho(E)$ is the density of exciton states. The set of quantities $\Delta E_1, \Delta \Omega_1$ is characterized by the dimensions of the region Γ_1 , and the same quantities with subscript 2 characterize the flux of frequency ω_2 . The five-dimensional region τ results from the occurrence of the δ function in (3.7).

Equation (4.2) gives the relation between the total number of excitons of frequency $\omega_1 + \omega_2$ arising per unit time in the crystal and the number of excitons in the primary fluxes. This is precisely the relation that is to be compared with experiment.^[1-3, 31, 35, 46] If we wish, we can derive a formula relating the energy fluxes, whereby we can find both the integral intensity and the intensity per unit energy interval.

Figure 3 illustrates the process of generation of a sum harmonic.

Now we shall study the concrete form of the quantity $Q(\dots)$, which is the matrix element of the operator equal to the sum of (2.1b) and (2.7b) for the transition characterized by the disappearance of the excitons ω_1 and ω_2 and the appearance of the exciton

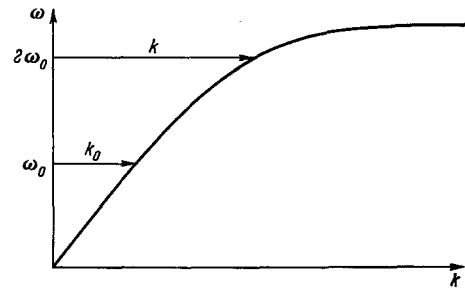


FIG. 3. Creation of an exciton of double frequency.

$\omega_1 + \omega_2$. The term $H_3^{II(3)}$ occurring in (2.7b) is important only in the X-ray region, as shown in^[19]. Since we are discussing the optical region, we can ignore it. Consequently, it suffices to limit ourselves to the sum of (2.9) and (2.1b), which must be written in terms of the variables ξ^+ and ξ in accord with the procedure described in the preceding chapter.

The matrix element (2.9) for the transition cited above has the form

$$H_3^{I(3)}(\rho_1, \rho_2, \rho_3, \mathbf{k}_1, \mathbf{k}_2) = \left(\frac{2\pi\hbar}{V}\right)^{3/2} N \frac{D_1 D_2 D}{\sqrt{\omega_1 \omega_2 (\omega_1 + \omega_2)}} \alpha_0(j_1, j_2, j, \mathbf{k}_1, \mathbf{k}_2), \quad (4.3)$$

where

$$\alpha_0 = \sum_{\mu_1 \mu_2} \left\{ \frac{(0|j_2|k_2, \mu_2)(\mu_2, k_2|j_1|k_1 + k_2, \mu_1)(0|j|k_1 + k_2, \mu_1^*)}{[E_{\mu_2}(k_2) - \hbar\omega_2] E_{\mu_1}(k_1) - \hbar(\omega_1 + \omega_2)} \right. \\ + \frac{(0|j|-k_1 - k_2, \mu_1)}{E_{\mu_1}(-k_1 - k_2) + \hbar(\omega_1 + \omega_2)} \\ \times \frac{(\mu_1, -k_1 - k_2|j_1|-k_2, \mu_2)(0|j_2|-k_2\mu_2)^*}{[E_{\mu_2}(-k_2) + \hbar\omega_2]} \\ \left. + \frac{(0|j_1|k_1\mu_1)(\mu_1 k_1|j|-k_2\mu_2)(0|j_2|-k_2\mu_2)^*}{[E_{\mu_1}(k_1) - \hbar\omega_1][E_{\mu_2}(-k_2) + \hbar\omega_2]} \right\}, \quad (4.4)$$

n is the refractive index of the crystal in the frequency region ω_1 , A_1 is determined from the condition (1.19), D_2 is the analogous characteristic of the frequency ω_2 , and D is that of the frequency $\omega_1 + \omega_2$. We must also add to Eq. (4.4) the same expression with the subscripts 1 and 2 interchanged. The vector \mathbf{l}_{j_1} determines the polarization of the flux characterized by frequency ω_1 , and \mathbf{l}_{j_2} that of frequency ω_2 , and \mathbf{l}_j that of frequency $\omega_1 + \omega_2$.

As is shown in^[20], the matrix element (2.1b) is generally small in comparison with the matrix element (2.9). Those cases are excluded in which the frequencies ω_1, ω_2 , and $\omega_1 + \omega_2$ happen to be in an exciton absorption region; then the cited matrix elements are comparable in order of magnitude. If we limit ourselves to precisely these resonance cases (see also Sec. 6), then the general, rather cumbersome expression for the matrix element of operator (2.1b) is simplified, and acquires the form (4.3), where we must substitute the following in place of

α_0 :

$$\alpha_1 = \sum_{\mu_1, \mu_2, \mu_3} V_{\mu_1 \mu_2 \mu_3}(\mathbf{k}_1, \mathbf{k}_1 + \mathbf{k}_2) \times \frac{(0 | j_1 | \mathbf{k}_1 \mu_1) (0 | j_2 | \mathbf{k}_2 \mu_2) (0 | j | \mathbf{k}_1 + \mathbf{k}_2, \mu_3)^*}{[E_{\mu_1}(\mathbf{k}_1) - \hbar \omega_1] [E_{\mu_2}(\mathbf{k}_2) - \hbar \omega_2] [E_{\mu_3}(\mathbf{k}_1 + \mathbf{k}_2) - \hbar (\omega_1 + \omega_2)]}, \quad (4.5)$$

where

$$V_{\mu_1, \mu_2, \mu_3}(\mathbf{k}, \mathbf{q}) = \sum_{s, f_1, f_2, f_3} V_{0, s}(f_3, 0, f_2, f_1) \times u_{f_1, \mu_1}(\mathbf{k}_1) u_{f_2, \mu_2}(\mathbf{q}) u_{f_3, \mu_3}(\mathbf{k} - \mathbf{q}) e^{i(\mathbf{k} - \mathbf{q}, \mathbf{r}_{0s})}. \quad (4.6)$$

Just as for (4.4), we must add to (4.5) the expression with "interchanged" subscripts 1 and 2.

Below we shall call the quantity $\alpha = \alpha_0 + \alpha_1$ the non-linear effect tensor.

First we shall take up the expression for α_0 , which resembles the non-linear polarization tensor introduced in [28-32]. This expression arises from the interaction between isolated molecules and radiation. It does not vanish, even if we completely neglect the interaction between the molecules, and it characterizes the non-linear effects on the basis of an oriented-gas model.

The tensor α_1 , which can be of the order of α_0 , is directly determined by the amount of interaction between the molecules. This tensor does not appear at all, in the studies known to the author, in line with the nature of the approximations made in these studies. Evidently, here the problem is the neglect of the anharmonicity occurring in the crystal independently of the radiation field.

We have discussed above the theory of the generation of sum harmonics; analogously we can also study such experimentally-observed phenomena as amplification by non-linear effects, [33] optical rectification, [34,35] and difference-frequency generation; [36,4] However, the previously published theory of these phenomena (see [35,37,38]) contains inaccuracies, which will be discussed in detail in Sec. 7.

5. The effect of symmetry and crystal dimensions on non-linear effects

The symmetry of the crystal imposes definite limitations on the form of the tensor α . In this sense the situation is analogous to that occurring in the study of the dielectric constant tensor [17] using symmetry theory (in particular, with spatial dispersion taken into account [13]), or the elasticity tensor, or the selection rules for dipole and quadrupole transitions in crystals, etc. The application of crystal-symmetry considerations in studying the tensor α is attractive in that the wave functions of the molecules (and this is even truer of crystals) are not known as a rule, and the calculation of the matrix elements entering into Eq. (4.4) is difficult.

At first we shall limit ourselves to studying the form of the tensor α_0 . The numerator of (4.4) con-

tains the product of three integrals of multiplicity τ , which can be written in the form of a single integral of multiplicity 3τ (τ is the dimensionality of the corresponding configuration space). The integral of multiplicity 3τ differs from zero only when the integrand contains a totally symmetric function. Let us subject all 3τ variables to a symmetry transformation. The 3τ -dimensional integral contains the sum of the squares of the moduli of the wave functions of the "intermediate" states, which transforms according to the totally symmetric representation. Consequently, the transformation properties of the "intermediate" states do not affect the transformation properties of the whole integrand. The properties of the latter are determined by the product $M_{j_1} M_{j_2} M_j$, where M_j is the projection of the vector \mathbf{M} on the direction l_j .

When the frequencies ω_1, ω_2 , and $\omega_1 + \omega_2$ are far from an absorption band, we can ignore the dependence of $E_\mu(\mathbf{k})$ on the direction of the vector \mathbf{k} . Then the tensor α_0 can be considered to be an ordinary third-order tensor, and in it the non-zero components are those that transform according to the totally symmetric representation.

It is not hard to find these non-zero components; this is done by a method analogous to that used in [39], where the form of the Raman-scattering tensor was found. We could also find the form of the tensor α_0 within the framework of the semiclassical theory (on this subject, see the notes, e.g., in [40,41]).

Table I gives the non-zero components of the tensor α_0 ; a 27-item table is shown for each group, and the common notation of the components is given at the top of the table. For the groups containing 3-, 4-, or 6-fold axes, the circular coordinates $\xi = x + iy$, $\eta = x - iy$ have been used. In this case, one must substitute $x \rightarrow \xi$, $y \rightarrow \eta$ at the top of the table. Wherever the table shows identical numbers, this means that the corresponding components are identical.

The symmetry properties of the tensor α_1 can be treated in an analogous way. The distinction from α_0 in treating it consists in the fact that here we must take into account the lattice sums (4.6). These sums can be treated by the method proposed by Born and Bradburn. [42] When the frequencies ω_1, ω_2 , and $\omega_1 + \omega_2$ are far from exciton absorption bands, we can neglect the variation of $E_\mu(\mathbf{k})$, and the non-zero components of the tensor α_1 are not identical with the corresponding non-zero components of α_0 . We should note, by the way, that as a rule α_0 exceeds α_1 when far from a resonance, except for special cases (see the preceding section).

We shall comment on the situation important in the non-linear effects that arises when even one of the frequencies ω_1, ω_2 , or $\omega_1 + \omega_2$ approaches an exciton absorption band. In this case, we generally cannot neglect the variation of $E_\mu(\mathbf{k})$. However,

Table I. Form of the non-linear effect tensor

Groups	xxx xxy xxz xyx xyx xzx xxz xzy xzx zzz	yxx yxy yxz yxx yxy yxz yxx yxy yxz zzz	xxx xxy xxz xyx xyx xzx xxz xzy xzx zzz	xyx xyx xzx xyx xyx xzx xyx xyx xzx zzz	Groups	xxx xxy xxz xyx xyx xzx xxz xzy xzx zzz	yxx yxy yxz yxx yxy yxz yxx yxy yxz zzz	xxx xxy xxz xyx xyx xzx xxz xzy xzx zzz	xyx xyx xzx xyx xyx xzx xyx xyx xzx zzz
C_2	0 0 1 0 0 2 3 4 0	0 0 5 0 0 6 7 8 0	9 10 0 11 12 0 0 0 13		C_{4v}	0 0 1 0 0 0 2 0 0	0 0 0 0 0 1 0 2 0	3 0 0 0 3 0 0 0 4	
C_s	1 2 0 3 4 0 0 0 5	6 7 0 8 9 0 0 0 10	0 0 11 0 0 12 13 14 0		D_4	0 0 0 0 0 1 0 2 0	0 0 1 0 0 0 2 0 0	3 0 0 0 3 0 0 0 4	
C_3	1 0 0 0 0 2 0 3 0	0 0 4 0 5 0 6 0 0	0 7 0 8 0 0 0 0 9		D_{2d}	0 0 0 0 0 1 0 2 0	0 0 -1 0 0 0 -2 0 0	3 0 0 0 3 0 0 0 4	
C_{2v}	0 0 1 0 0 0 2 0 0	0 0 0 0 0 3 0 4 0	6 0 0 0 7 0 0 0 8		D_6	0 0 0 0 0 1 0 2 0	0 0 -1 0 0 0 -2 0 0	0 3 0 -3 0 0 0 0 4	
D_2	0 0 0 0 0 1 0 2 0	0 0 3 0 0 0 4 0 0	0 5 0 6 0 0 0 0 0		C_{6v}	0 0 0 0 0 1 0 2 0	0 0 1 0 0 0 2 0 0	0 3 0 0 3 0 0 0 4	
C_{3v}	1 0 0 0 0 2 0 3 0	0 0 2 0 1 0 3 0 0	0 4 0 0 0 0 0 0 5		D_{3h}	1 0 0 0 0 0 0 0 0	0 0 0 0 1 0 0 0 0	0 0 0 0 0 0 0 0 0	
D_3	1 0 0 0 0 2 0 3 0	0 0 -2 0 1 0 -3 0 0	0 4 0 -4 0 0 0 0 5		T	0 0 0 0 0 1 0 2 0	0 0 1 0 0 0 2 0 0	0 1 0 0 2 0 0 0 0	
C_4	0 0 0 0 0 1 0 2 0	0 0 4 0 0 0 6 0 0	0 7 0 8 0 0 0 0 9		T_d	0 0 0 0 0 1 0 1 0	0 0 1 0 0 0 1 0 0	0 1 0 1 0 0 0 0 0	
S_4	0 0 0 0 0 1 0 2 0	0 0 4 0 0 0 6 0 0	0 7 0 8 0 0 0 0 9		O	0 0 0 0 0 1 0 -1 0	0 0 1 0 0 0 -1 0 0	0 1 0 -1 0 0 0 0 0	
C_6	0 0 0 0 0 0 0 2 0	0 0 4 0 0 0 6 0 0	0 7 0 8 0 0 0 0 9						

evidently the taking into account of the variation of $E_\mu(\mathbf{k})$ does not affect the vanishing of the components of the tensor α . This is due to the fact that the vanishing of the tensor α requires only the vanishing of the numerators of the terms entering into the summations of (4.4) and (4.5), independently of the magnitude and direction of \mathbf{k} . Taking into account the variation of $E_\mu(\mathbf{k})$ can alter somewhat the values of the non-zero components of the tensor α . In particular, generally speaking, those components come to differ that had been equal when the variation of $E_\mu(\mathbf{k})$ was neglected. This fact is of definite interest, since it can generally be used to study the variation of $E_\mu(\mathbf{k})$ by observation of non-linear effects near exciton absorption bands.

The intensity of the non-linear effects depends considerably on the dimensions of the crystal. For a crystal of finite dimensions, the matrix element of the transition has the form

$$H' = DV^{-3/2}\alpha f(\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}), \quad (5.1)$$

where D is a quantity of no particular interest in this case, V is the volume of the crystal, α is the non-linear effect tensor,

$$f(q) = \sum_s e^{i(\mathbf{q}\cdot\mathbf{r}(s))}, \quad (5.2)$$

\mathbf{k}_1 and \mathbf{k}_2 are the wave vectors of the primary fluxes, and \mathbf{k} of the resultant flux; the summation in (5.2) is performed over the crystal.

Since the intensity of the non-linear process is proportional to the square of the modulus of the matrix element, we must further find $|f|^2$. For this, we must now know the shape of the crystal. We shall assume that it has been cut in the form of a plate, and the vectors \mathbf{k}_1 , \mathbf{k}_2 , and \mathbf{k} are perpendicular to its faces. Since the vector \mathbf{k} in (5.2) is small, we can go over from summation to integration. Then we find that the intensity I of the resultant flux depends on the crystal thickness x according to the formula*

$$I \sim |f|^2 \sim \frac{\sin^2 \frac{\Delta k x}{2}}{(\Delta k)^2}, \quad (5.3)$$

where $\Delta \mathbf{k} = \mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}$.

Equation (5.3) implies that in order to increase the intensity of a non-linear effect, it is expedient to choose conditions such that Δk is small. In the experimental study^[43], an appreciable increase was

*An oscillating relation of this type occurs only when the imaginary parts of the wave vectors \mathbf{k}_1 , \mathbf{k}_2 , and \mathbf{k} characterizing the attenuation are small. In the opposite case a number of peculiarities arise (see^[12a]).

thus attained in the intensity of a sum harmonic.

The quantity Δk characterizes the degree of "conservation" of quasimomentum $\hbar k$ of the exciton in the non-linear process. In an infinite crystal ($x = \infty$), non-linear effects are possible (see (5.3)) only when

$$\Delta k = 0,$$

i.e.,

$$k = k_1 + k_2.$$

When $x < \infty$, the maximum in I corresponds to $\Delta k \neq 0$. The greater Δk is, the greater the deviation from the conservation law. It is interesting to note that Eq. (5.3) allows of the following graphic interpretation. We shall assume that a certain fictitious wave vector Δk is being propagated through the crystal.

The intensity maxima of the non-linear effect appear when a half-integral number of such waves is superimposed in the crystal; in essence, Eq. (5.3) is the interference condition for this wave.

Equation (5.3) was first derived in [44] and confirmed experimentally in [45]. Here light of frequency ω_0 from a laser fell on a plane-parallel plate. By rotating the latter they could vary the path length x traversed by the light in the crystal. As a result they observed the intensity of the sum harmonic of frequency $2\omega_0$ to be an oscillating function of the rotation angle of the plate.

We shall mention also the experimental study [46], where they attained a variation in the intensity of a sum harmonic arising from the fact that the selection rules differ with differing orientations of the crystal.

6. Resonance Phenomena

This section will discuss some peculiarities of the non-linear effects as the frequencies ω_1 , ω_2 , and $\omega_1 + \omega_2$ approach exciton absorption bands. We shall limit ourselves at first to discussing only the tensor α_0 .

For concreteness, we shall assume that ω_2 is approaching an absorption band, while ω_1 and $\omega_1 + \omega_2$ are far from exciton absorption bands. Then the following factor entering into (4.4) approaches infinity:

$$[E_{\mu_2}(\mathbf{k}_2) - \hbar\omega_2]^{-1} \tag{6.1}$$

However, this fact does not lead to any complications, since the quantity D_2 entering into (4.3) approaches zero, and just compensates for the infinity arising from (6.1). After performing calculations analogous to [47], we find that the matrix element (4.3) depends on ω_2 according to the formula:

$$H = C \{ |E_{\mu}(\mathbf{k}_2) - \hbar\omega_2|^2 + |T(\mathbf{q}j\mu)|^2 \}^{-1/2}, \tag{6.2}$$

where the coefficient C contains all the quantities that depend relatively weakly on ω_2 .

We can treat analogously the cases in which ω_1 or $\omega_1 + \omega_2$ is near an exciton absorption band. Thus, the matrix element (4.3) remains finite for any values of the frequencies ω_1 and ω_2 .

By a suitable choice of ω_1 and ω_2 , we can considerably increase the intensity of a non-linear effect. This last remark requires the following qualification. We should not suppose that we must invariably get an increase in the intensity of the non-linear process when one of the cited frequencies approaches an intense absorption band. In order to understand this, let us examine some of the features of Eq. (4.4). Each term entering into the double summation of (4.4) involves a set of three transitions that we can schematically refer to as $0 \rightarrow 1$, $1 \rightarrow 2$, and $2 \rightarrow 0$ (Fig. 4). It can happen that the transition $0 \rightarrow 1$ has a high probability, while the transitions $1 \rightarrow 2$ and $2 \rightarrow 0$ have low probability. Then, as the frequency ω_2 approaches the frequency Ω_{01} of intense absorption, we will not get the increase in intensity of the non-linear effect that we would expect at first glance.

Probably, this is precisely the situation involved in the results of the experiments of [48], where they studied the effect of approach of the frequency of the primary radiation to an absorption band, and observed no appreciable increase in the intensity of the non-linear effect. In this case, the resonance mentioned above proves to be poorly marked.

We must make another remark on Eq. (6.2). The latter was derived under the assumption that the imaginary part of $E_{\rho}(\mathbf{k})$ satisfies the condition

$$\gamma = \text{Im} E_{\rho}(\mathbf{k}) \ll T(\mathbf{k}j\mu). \tag{6.3}$$

If (6.3) is not satisfied, we must have recourse to Eq. (4.4), and consider ω_1 , ω_2 , and $\omega_1 + \omega_2$ to be complex quantities.

We can also consider in an analogous way the behavior of the tensor α_1 in the resonance case; no singularities appear here as well, whereas (taking into account what we have said above) the tensor α_1 attains one of its maxima.

Let us assume that $\omega_1 = \omega_2 = \omega_0$ and examine the situation in which the frequency ω_0 lies in the region of an absorption band. Just as in the previously discussed case, the quantity α_1 also increases along

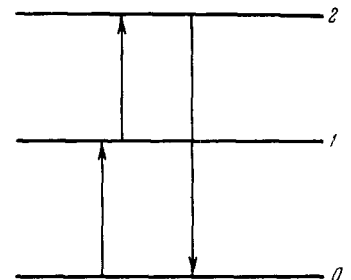


FIG. 4. Diagram of the transitions involved in the matrix element (4.3).

with the intensity of the non-linear combination process. As we have stated, a wave of frequency $2\omega_0$ is formed through the combination process. Since here the number of excitons of frequency ω_0 decreases, the process under discussion is an absorption process due to a third-order non-linear interaction with respect to the excitons of frequency ω_0 .

Consequently, the amount of absorption must depend on the intensity of the incident radiation (so-called induced absorption). The experimental study^[6] has shown that the absorption cross-section in liquid CS_2 for radiation of $\lambda = 6943 \text{ \AA}$ depends on the intensity I of the incident radiation according to the formula

$$\sigma = \sigma_0 + \sigma_1 I,$$

where σ_0 and σ_1 are constants. An analogous relation must also hold for crystals. However, we know of no pertinent experiments. The theory of induced absorption is discussed in further detail in^[128].

The absorption process described above is called two-photon absorption, since the act of absorption consists in the simultaneous disappearance of two photons in the medium (excitons). We can consider the luminescence associated with two-photon absorption as though it resulted from the flux of excitons produced by the non-linear process within the crystal. Thus, in^[50] they studied experimentally a $\text{CaF}_2 : \text{Eu}$ crystal irradiated by the line $\lambda = 6943 \text{ \AA}$, while the luminescence occurred at the wavelength $\lambda = 4250 \text{ \AA}$. A luminescence of the same type in anthracene was studied in^[49], while in^[51] a mechanism involving triplet excitons was adduced to explain some characteristics of the cited luminescence.

Let us consider the case in which $\omega_1 \neq \omega_2$, and the primary exciton fluxes are equal respectively to I_1 and I_2 . Then an interesting feature of the induced absorption of the flux at ω_1 will be the proportionality between this absorption and I_2 ; I_2 shows an analogous characteristic with respect to I_1 .

Now let us assume that an intense (laser) light flux I_1 is incident on the crystal; we choose its frequency ω_1 such that the flux I_1 is not absorbed.

Let us permit the crystal to be simultaneously irradiated with an additional illumination I_2 of frequency ω_2 , which we choose so that $\omega_1 + \omega_2$ or $\omega_1 - \omega_2$ falls within an absorption band. Then the flux I_1 and also the flux I_2 can be absorbed. Thus, in^[129] they observed experimentally the relation of the absorption of the flux I_2 to the frequency ω_2 . Here they could get information on the distribution of the excited states.

The absorption of primary excitons of frequency ω_0 occurs not only in combination, but also in decay. Let the crystal have an absorption band in the region $\omega_0/2$. The decay obeys the law of conservation of the wave vector $\mathbf{k}_0 = \mathbf{k}_1 + \mathbf{k}_2$, and although \mathbf{k}_0 is small, \mathbf{k}_1 and \mathbf{k}_2 can be large (Fig. 5). The latter fact re-

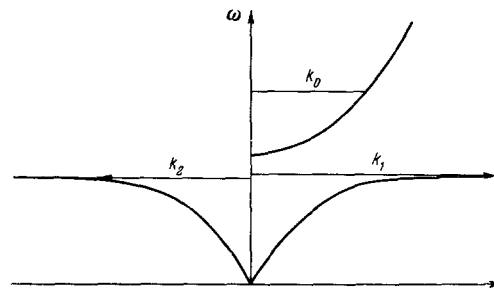


FIG. 5. Diagram of the decay of an exciton of wave vector \mathbf{k}_0 into two excitons of wave vectors \mathbf{k}_1 and \mathbf{k}_2 .

sults in a higher density of final states, and hence a higher probability of decay. The probability of disappearance of an exciton of frequency ω_0 leads to the appearance of an absorption band in this spectral region; as was shown in^[52], the value of this absorption is comparable with that of the absorption in the region $\omega_0/2$. In the experimental studies^[53,54], they studied the LiF crystal, and observed absorption in the far ultraviolet at 25 eV. This absorption was interpreted in^[55] as the simultaneous excitation of two Coulombic excitons. Absorption bands have also been observed in the oxygen crystal with frequencies equal to the sum of frequencies observed in gaseous oxygen.^[56]

7. Some remarks on the existing methods of calculating non-linear effects

The theory of non-linear effects has also been developed by using methods differing from those presented in the previous sections. It is of definite interest to compare these methods, as we shall do in this section.

We shall first discuss the theory of non-linear effects^[57] developed on the hypothesis that the interaction between the crystal and the radiation can be treated as a small perturbation, the radiation field being quantized. The most essential defects of this approach consist in the following.

As we have seen above, two mechanisms contribute to the intensity of a non-linear process: anharmonicity involving the interaction between the radiation field and the crystal, and anharmonicity existing in the Coulombic subsystem. Furthermore, anharmonicity in the Coulombic subsystem was not taken into account in^[57]. We should not suppose that it is generally impossible to take it into account by the method of small perturbations; it is taken into account in the higher approximations. Besides, in the method outlined in the preceding sections, anharmonicity of the Coulombic subsystem is taken into account even in the first approximation of the perturbation theory. We must also note that the method of small perturbations and the method used in the preceding sections give results for the non-linear effect tensor that

differ numerically from one another by a factor of 2–3.

The reason for this discrepancy consists in the following. As we have seen above (see Sec. 2), the exciton-photon interaction gives rise in the Hamiltonian to both quadratic and cubic terms in the creation and annihilation operators. The non-linear effects arise from only that part of the complete Hamiltonian that appears in the form of anharmonic terms. Hence, in considering all exciton-photon interactions as perturbations, we commit an error if the quadratic part makes an appreciable contribution to the magnitude of the exciton energy.

Hence, the method of small perturbations can be applied only when the cited quadratic terms make no appreciable correction to the spectrum, i.e., only for a gas.

We note also that the method of small perturbations gives resonance denominators [see Eq. (6.1)] that make the non-linear effect tensor infinite when the frequencies ω_1 , ω_2 , or $\omega_1 + \omega_2$ approach an absorption band of the crystal. This involves an incorrect choice of the functions of the zero-order approximation. In order to liquidate these singularities, we could seemingly use the Weisskopf-Wigner method.*^[58] In actuality, we might encounter difficulties here in studying closely-spaced levels. We can also avoid the singularities by introducing a complex value for the exciton energy^[59] due to the existence of radiationless transitions (see Eq. (6.3) and the following discussion).

However, as we have seen, the problem of singularities does not arise at all within the framework of the theory developed above.

We also note that there is a theory of non-linear effects (see^[28-32,60-69]) in which the radiation field is treated as unquantized. We have already discussed it above (see the Introduction). As we have mentioned, the fundamental problem of the theories presented in these studies is to find the quantity β , which is called the non-linear polarizability. We can divide these studies into three groups.

The first group^[28-32] are studies in which the peculiarities of the condensed medium are not taken into account at all, or are taken into account by highly imperfect means. Thus, for example, in^[30] the treatment is carried out at first for a gas. Then an effective field is substituted for the external field by multiplying the value of the external field by some coefficient. Such a procedure does not permit one to take into account one of the fundamental properties of a crystal, its anisotropy.

The second group of studies^[65-70] takes into account the peculiarities of the crystalline medium more systematically from the outset. However, even

this group of studies does not take into account the contribution made by anharmonicity of the Coulombic subsystem. The latter is highly essential in studying non-linear effects in the vicinity of exciton absorption bands, as well as in cases in which the contribution made by the tensor α_0 is small.

Further, in these studies the behavior of the intensity of the non-linear effects near a resonance is determined by the magnitude of the Coulombic-exciton attenuation γ (when $\gamma = 0$, then the intensity at the resonance generally approaches infinity). This completely ignores the possible case in which γ is small, and the cited behavior is determined by the value of T (see the preceding section). In^[70], they introduced a parameter Γ characterizing the non-adiabaticity of the inclusion of the interaction between the crystal and the radiation in order to remove the singularity at the resonance. However, the authors of^[70] do not state how Γ is expressed in terms of the characteristics of the crystal or any other quantities.

The authors of the third group of studies^[60-64] limit themselves to studying the problem phenomenologically; the problem is not raised at all in these studies of finding β in concrete form. We shall not spend time on these studies.

III. NONLINEAR EFFECTS DUE TO ELECTRONIC-VIBRATIONAL INTERACTION (RAMAN SCATTERING)

8. The general theory of Raman scattering

As was mentioned in Chapter I, another of the non-linear effects is effectuated by electronic-vibrational interaction, namely, Raman scattering. It is due to the interaction of light waves with intramolecular acoustic and optical vibrations.

We shall first discuss scattering due to intramolecular vibrations, and limit ourselves to discussing the Stokes component of the Raman spectrum. We can conveniently illustrate the process giving rise to it by the diagram shown in Fig. 6. In the initial state, let there be an exciton of wave vector \mathbf{k}_0 and frequency ω_0 lying in the visible.* This exciton is transformed into two excitons. The first, having a wave vector \mathbf{k}_1 and frequency ω_1 , also lies in the visible. Upon emerging from the crystal, it gives rise to the Stokes component of the Raman spectrum. The second exciton, having a wave vector \mathbf{k}_2 and frequency ω_2 , lies in the frequency range of the intramolecular vibrations, and is subsequently transformed into heat. Since Raman scattering is usually observed at a right angle (Fig. 7), the vectors \mathbf{k}_1 , \mathbf{k}_2 , and \mathbf{k}_0 are about of the same length. These

*Insofar as the author knows, this method has not been applied to study non-linear effects.

*For technical reasons, Raman scattering is usually studied in the visible. However, this limitation is not essential in theory.

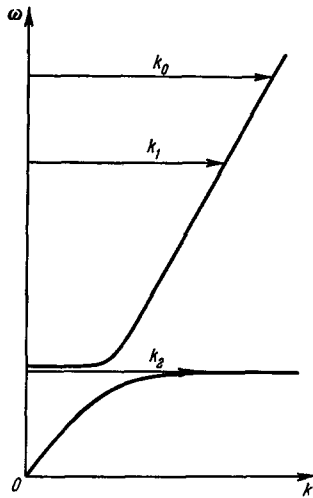


FIG. 6. Diagram of the generation of the Stokes component of the Raman spectrum.

vectors are shown in Fig. 6 with this fact taken into account.

Let us assume that the intensity of the scattered radiation does not attain such a value that laser action results. By applying the method used in Sec. 4 (for further detail, see [77]), we find that the intensity of the scattered radiation of polarization j and wave vector k_1 is equal to

$$I_j(\mathbf{k}_1) = \frac{n_j^2}{c^3} \frac{\omega_1^2}{\omega_0^2} N D(j, \mathbf{k}_1) \sum_{j'} D(j', \mathbf{k}_0) |a_{j'j}|^2 \left(\frac{\partial \omega}{\partial \mathbf{k}} \right)_{j'} I_{0j'}, \quad (8.1)$$

where c is the velocity of light, $I_{0j'}$ is the intensity of the exciton flux determining the incident radiation of polarization j' , $\partial \omega / \partial \mathbf{k}$ is the group velocity of this flux, ω_0 is the frequency of the incident radiation, and ω_1 that of the scattered radiation; the other symbols have already been used in (4.3).

The tensor $a_{j'j}$ consists (cf. Sec. 4) of two terms:

$$a_{j'j} = a_{j'j}^{(0)} + a_{j'j}^{(1)},$$

where

$$a_{j'j}^{(0)} = \sum_{\mu} \left\{ \frac{(0|j'| \mathbf{k}_0, \mu)(\mu, \mathbf{k}_0 | j | \mathbf{k}_0 - \mathbf{k}_1, \mu')}{E_{\mu}(\mathbf{k}_0) - \hbar \omega_0} + \frac{(0|j | -\mathbf{k}_1, \mu)(\mu, -\mathbf{k}_1 | j' | \mathbf{k}_0 - \mathbf{k}_1, \mu')}{E_{\mu}(-\mathbf{k}) + \hbar \omega_1} \right\}, \quad (8.2)$$

$$a_{j'j}^{(1)} = \sum_{\mu_1, \mu_2} \left\{ \frac{(0|j' | \mathbf{k}_0 \mu_1) V_{\mu_1 \mu_2 \mu'}(\mathbf{k}_1 \mathbf{k}_0) (0|j | \mathbf{k}_1, \mu_2)^*}{E_{\mu_1}(\mathbf{k}_0) - \hbar \omega_0} + \frac{(0|j | -\mathbf{k}_1, \mu_2) V_{\mu_1 \mu_2 \mu'}(-\mathbf{k}_0, -\mathbf{k}_1) (0|j' | -\mathbf{k}_0, \mu_1)^*}{[E_{\mu_1}(-\mathbf{k}) + \hbar \omega_1][E_{\mu_2}(-\mathbf{k}_0) + \hbar \omega_0]} \right\}, \quad (8.3)$$

$$V_{\mu_1, \mu_2, \mu_3}(\mathbf{k}_1, \mathbf{k}_2) = \sum_{n, f_1, f_2, f_3} V_{n0}(f_2, f_1, 0, f_3) u_{f_1, \mu_1}^*(\mathbf{k}_1) u_{f_2 \mu_2} \times (\mathbf{k}_2) u_{f_3, \mu_3}(\mathbf{k}_2 - \mathbf{k}_1) e^{i(\mathbf{k}_2 - \mathbf{k}_1 \cdot \mathbf{r}_{n0})}. \quad (8.4)$$

and μ' is the number of the branch manifested in the Raman spectrum.

Equation (8.2) for the tensor $a^{(0)}$ is an analog of the formula for the Raman scattering tensor in gases, and to some extent it characterizes the scattering in

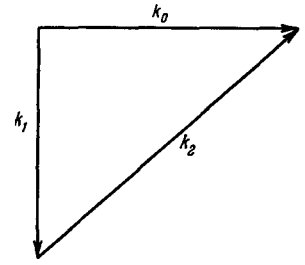


FIG. 7. Arrangement of the wave vectors in Raman scattering at an angle of $\pi/2$.

terms of an oriented-gas model. Hence, for brevity we shall refer below to tensor (8.2) as the ordinary tensor.

Now we shall discuss Eq. (8.3) for the tensor $a^{(1)}$ in more detail, and for concreteness we shall limit ourselves to dipole-dipole interaction between the molecules. Expression (8.3) differs from zero only when the dipole moment of the virtual electronic transition interacts with the dipole moments of those vibrations of the neighboring molecules that are manifested in the Raman spectra. This means that (8.3) differs from zero for vibrations that are active simultaneously in the infrared and Raman spectra. These vibrations can exist only in piezoelectric crystals, which lack centers of inversion. Therefore we shall call tensor (8.3) the piezoelectric tensor, in distinction from the ordinary tensor (8.2). Understandably, in a piezocrystal not all the vibrations make a big contribution to the piezoelectric tensor, but only those for which the dipole moment differs from zero.

Thus the vibrations lacking a dipole moment are characterized by the Raman-scattering tensor (8.2), and the vibrations having a dipole moment by the sum of (8.2) and (8.3). In conclusion, we shall take up some other variants of the theory of Raman scattering in crystals.

Reference [78] treated Raman scattering in a crystal by the method of small perturbations; the difference between the latter method and that used above has been discussed in Sec. 7, and there is no need to repeat it here. Studies [59, 79] have recently appeared in which Raman scattering has been treated by using the density matrix. A highly valuable feature here is the account taken of attenuation involving radiationless transitions. However, even these studies assumed the interaction between the material and the radiation to be small. Further, we note that Strizhevskii et al. [80] tried to treat Raman scattering from the standpoint of the exciton theory. Here the role of the Hamiltonian of the zero-order approximation was played by the Hamiltonian of the field of normal waves in the medium (i.e., the fact was taken into account that $n \neq 1$). However, at the same time, the perturbation was taken to be H_{int} , or all the interactions between the transverse photons and the Coulombic subsystem. The matrix elements of H_{int} were taken in terms of the wave functions of the

Hamiltonian of the zero-order approximation. However, this Hamiltonian already partially contains H_{int} . That is, the same operator was used in [80] both in the Hamiltonian of the zero-order approximation (in an implicit form) and in the perturbation. Such a procedure at least requires justification. We also note that Strizhevskii [80] did not derive the portion of the Raman-scattering tensor due to the presence of anharmonicity in the Coulombic Hamiltonian. As we have seen above, its contribution is quite substantial.

By using the method presented in Sec. 5, we can also treat the effect of the crystal dimensions on the Raman scattering intensity. From the calculations, we find that the Raman scattering intensity depends on the crystal dimensions according to a formula analogous to (5.3). Here, however, $|\Delta\mathbf{k}| = |\mathbf{k}_0 - \mathbf{k}_1| - |\mathbf{k}_2|$; \mathbf{k}_0 is the wave vector of the primary radiation; \mathbf{k}_1 that of the scattered radiation; $E_{\rho_2}(\mathbf{k}_2) = E_{\rho_0}(\mathbf{k}_0) - E_{\rho_1}(\mathbf{k}_1)$ is the condition determining \mathbf{k}_2 ; the vector $\Delta\mathbf{k}$ lies along $\mathbf{k}_0 - \mathbf{k}_1$; and x is the thickness of the crystal, which is cut in the form of a plate having surfaces perpendicular to the vector $\mathbf{k}_0 - \mathbf{k}_1$.

We should note that in order to observe an oscillating dependence of (5.3) on the crystal thickness, we must strictly fix \mathbf{k}_1 and \mathbf{k}_0 . This means that the primary radiation must be strictly monochromatic, and the receiver must contain an apparatus of high resolving power.

If these conditions are not obeyed, the effect will be "smeared out." Insofar as we know, this effect has not been observed experimentally yet.

The Mandelstam-Brillouin components in the Rayleigh scattering arise from the excitation of acoustic vibrations in the crystal.

The process of generation of the "red" component can be represented by the following scheme. The initial exciton of frequency ω_0 decays into two: an exciton of frequency ν belonging to the acoustic branch, and an exciton whose frequency ω_1 is only a little smaller than ω_0 ($\omega_0 = \omega_1 + \nu$).

The intensities of the Mandelstam-Brillouin components were found within the framework of the exciton theory in [81]. As a result, a formula was derived similar to Eq. (8.1); however, instead of the tensor $a_{j'j}$ one must use the tensor

$$a_{j'j} = (\sigma_1 + \sigma_2 + \sigma_3)(\mathbf{k}_1 - \mathbf{k}_0, \mathbf{y}_r(\mathbf{k}_1 - \mathbf{k}_0)), \quad (8.5)$$

where

$$\sigma_1 = \sum_{\mu} \left\{ \frac{(0|j'| \mathbf{k}_0, \mu)(0|j| \mathbf{k}_1, \mu)^*}{E_{\mu}(\mathbf{k}_0) - \hbar\omega_0} + \frac{(0|j| - \mathbf{k}_1, \mu)(0|j' - \mathbf{k}_0, \mu)^*}{E_{\mu}(-\mathbf{k}_1) + \hbar\omega_1} \right\}, \quad (8.6)$$

*Just as in deriving Eq. (5.3), it is also necessary here that the attenuation of the waves should be small. This occurs only at very low scattering angles ("forward" scattering). In the converse case there will be no oscillating relation.

$$\sigma_2 = \sum_p \frac{e_p^2}{m_p} (\mathbf{l}_j, \mathbf{l}_{j'}), \quad (8.7)$$

$$\sigma_3 = \sum_{\mu_1\mu_2} \left\{ \frac{(0|j'| \mathbf{k}_0, \mu_1) E_{\mu_1\mu_2}(\mathbf{k}_1, \mathbf{k}_0)(0|j| \mathbf{k}_1, \mu)^*}{[E_{\mu_1}(\mathbf{k}_0) - \hbar\omega_0][E_{\mu_2}(\mathbf{k}_1) - \hbar\omega_1]} + \frac{(0|j'| - \mathbf{k}_0, \mu_1)^* E_{\mu_1\mu_2}(-\mathbf{k}_0, -\mathbf{k}_1)(0|j| - \mathbf{k}_1, \mu_2)}{[E_{\mu_1}(-\mathbf{k}_0) + \hbar\omega_0][E_{\mu_2}(-\mathbf{k}_1) + \hbar\omega_1]} \right\}, \quad (8.7')$$

$$E_{\mu_1\mu_2}(\mathbf{k}_1, \mathbf{k}_2) = \sum_j E_j u_{j\mu_1}^*(\mathbf{k}_1) u_{j\mu_2}(\mathbf{k}_2), \quad (8.8)$$

$y_r(\mathbf{k})$ are the coefficients of the transformation from translational displacements to the displacements involved in the r -th acoustic vibration, [81] and the notation in (8.2) has also been adopted.

The term σ_1 and σ_2 are a generalization of the formula for the Rayleigh scattering tensor in gases (see, e.g., Eq. (9.11) of the monograph [22]). However, the term σ_3 is characteristic only of a crystal. It is due to anharmonicity in the Coulombic subsystem, and has not been previously discussed. We can show that [81]

$$\frac{\sigma_1}{\sigma_3} \sim \frac{E_{\mu} - \hbar\omega_0}{E_{\mu}}. \quad (8.9)$$

Hence, in general, the terms σ_3 are not small in comparison with σ_1 and σ_2 (σ_1 and σ_2 are quantities of about the same order of magnitude). As we can see from (8.9), the role of σ_3 increases as the frequency of the incident light approaches an absorption band. Thus, by studying the relation of the intensity of the Rayleigh scattering to the frequency ω_0 of the incident light, we can get information on the anharmonicity in the electronic subsystem as well.

We shall now proceed to the problem of calculating the intensity of the undisplaced component of the Rayleigh scattering. As is known, [82] an ideal crystal with fixed equilibrium positions of the molecules gives no undisplaced component. The latter arises only from thermal fluctuations, and also from various deviations of the structure from ideality, which we can consider to be the cause of the scattering. "Extra" molecules, vacancies, and lattice-deformation regions can act as the structural defects. By finding the scattering from a deformed structure, we thus solve the problem of the scattering due to thermal fluctuations, since the latter can be considered as regions of the crystal that have undergone a certain expansion or compression. By calculations analogous to those giving rise to Eq. (8.5), we can show that the intensity of the undisplaced component is determined by the tensor (8.5) within the accuracy of an insignificant constant. In this tensor, the following function replaces $(\mathbf{k}_0 - \mathbf{k}_1, \mathbf{y}_r(\mathbf{k}_0 - \mathbf{k}_1))$:

$$f = N^{-1/2} \sum_s' e^{i(\mathbf{k}_0 - \mathbf{k}_1, \mathbf{r}_s)} - \sum_s'' e^{i(\mathbf{k}_0 - \mathbf{k}_1, \mathbf{r}_s)} + \sum_s''' (\mathbf{u}_s, \mathbf{k}_0 - \mathbf{k}_1) e^{i(\mathbf{k}_0 - \mathbf{k}_1, \mathbf{r}_s)}, \quad (8.10)$$

where Σ' is the summation over the "extra" mole-

cules, Σ'' over the vacancies, Σ''' over the displaced molecules, and \mathbf{u}_s is the displacement of the s -th molecule. We see that f characterizes the deviation of the crystal from ideality. In order to calculate f , we must assign a concrete distribution of the extra molecules and vacancies, and also assign the displacements \mathbf{u}_s .

Raman scattering due to optical intermolecular vibrations can also be treated analogously. If here we limit ourselves to dipole-dipole interaction between the molecules, then the Raman-scattering tensor for the above-cited vibrations is determined by Eq. (8.6). However, in the latter we must set $\sigma_1 = \sigma_2 = 0$, and instead of $E_{\mu_1\mu_2}(\mathbf{k}_1, \mathbf{k}_2)(\mathbf{k}_0 - \mathbf{k}_1, \mathbf{y}_r(\mathbf{k}_0 - \mathbf{k}_1))$ we must use the expression

$$V_{\mu_1\mu_2}(\mathbf{k}_1, \mathbf{k}_0) = \sum_{s_1/s_2} V_{0s}^{x_1x_2}(f_1, f_2) u_{f_1\mu_1}^*(\mathbf{k}_1) u_{f_2\mu_2}(\mathbf{k}_2) \times \{y_r(\mathbf{k}_2 - \mathbf{k}_1, x_1) e^{i(\mathbf{k}_2, \mathbf{r}_s)} - y_r(\mathbf{k}_2 - \mathbf{k}_1, x_2) e^{i(\mathbf{k}_1, \mathbf{r}_s)}\}. \quad (8.11)$$

Here r is the number of the branch, x_1 and x_2 are the numbers of the Cartesian coordinates of the displacements of the molecules, and the $y(\dots)$ are the transformation coefficients from Cartesian variables to the crystal variables (e.g., one can find expressions for them in [83]).

Thus, the Raman scattering tensor for the intermolecular vibrations depends on the frequency of the incident light in a way differing from the ordinary tensor (8.2) (which is analogous to the Raman-scattering tensor in gases), but resembling the piezoelectric tensor (8.3). As we see from (8.11), the latter is determined by the intensity of the intermolecular interactions, and vanishes when they are neglected. We recall that the ordinary tensor depends weakly on the intermolecular interactions: in essence, as we have said, it characterizes the Raman scattering in an oriented gas.

Recently lasers have made it possible to observe the so-called stimulated Raman scattering. A review [84] has been devoted to this problem, but nevertheless we shall point out here how one should treat this phenomenon within the framework of the exciton theory (such a treatment has been made in [85]).

When the intensity of the primary radiation is high, the scattered radiation will also be very intense. This leads to an increase in the occupation quantum numbers $n(\rho_1, \mathbf{k}_1)$ that enter into Eq. (3.8) and determine the intensity of the secondary radiation. According to this formula, the increase in $n(\rho_1, \mathbf{k}_1)$ raises the probability of transition from the initial to the final state. Hence, a crystal in which Raman scattering takes place becomes the generator of a new frequency.

The Mandelstam-Brillouin components can also give stimulated emission; this phenomenon has been experimentally observed in [86].

Similarly to induced optical absorption due to the exciton-combination effect (see Sec. 6), we can have

induced absorption due to Raman scattering. In [87], induced absorption was observed, which proved to be proportional to the intensity of the stimulated Raman scattering; this fact indicates that the induced absorption is directly due to the Raman scattering.

We note also that in the experimental study [88] they observed Raman scattering accompanied by the formation of an electronic excited state, or electronic exciton, rather than a vibrational excited state, as usually occurs in Raman scattering. From the viewpoint applied in this paper for classifying effects, this phenomenon belongs to the electronic effects. However, its treatment is fully analogous to that of Raman scattering due to the intramolecular vibrations.

9. The form of the Raman-scattering tensor. Harmonics. Combination frequencies. Fermi resonance. Temperature-dependence

This section will take up the form of the Raman-scattering tensor (RST) by group-theoretical methods. It is evident here that the higher the symmetry of the crystal is, the more essential the results obtained by symmetry theory. We note that one observes experimentally not the components of the RST themselves, but the so-called two-dimensional intensity table. [89] In order to determine it, we must study the intensities of the scattered light with varying orientations of the polarizers in the detector and the illuminator. Thus, for example, the b_{xx} component of this table characterizes the intensity of the scattered radiation under the condition that the polarizers of the detector and the illuminator are oriented along the x axis. Here, as we have said, the scattering angle is taken equal to $\pi/2$. One defines analogously the eight other components of this table (as can be easily seen, the table contains nine components in all). We must take the moduli of the squares of the corresponding components of the RST for theoretical determination of the components of this table. Whenever a vibration manifested in the Raman spectra is degenerate, the component in the intensity table is obtained by summing the corresponding moduli.

Studies are known (see, e.g., [89]) in which the form of the Raman-scattering tensor has been treated within the framework of the highly approximate polarizability theory. We shall not have recourse to this theory in this review; the form of the tensor will be studied on the basis of the exact expressions (8.2) and (8.3). The ordinary tensor (8.2) will be studied by group-theory methods in this section, and the piezoelectric tensor (8.3) in Sec. 10.

Since the appropriate procedure is analogous to that presented above (see Sec. 5), we shall not take it up here, but proceed directly to studying the characteristic features of Raman scattering of light in crystals.

When the frequency of the incident light approaches an absorption band (the resonance case), one of the

terms of the summation (8.2) becomes much larger than the others, which we can thereby neglect.

The results of the group-theoretical study of the RST are shown in Table II for the groups of the crystal classes not containing an inversion center. In centric crystals, only the vibrations symmetric with respect to inversion (gerade) make a contribution to the RST in the dipole approximation. Hence, the form of the RST in a centric crystal turns out to be the same as if the crystal did not contain the inversion center.

The form of the RST for the resonance case depends on the symmetry properties of the final and intermediate states. Hence, by studying the form of the RST, we can study the symmetry properties of the exciton states.

Tables II gives the irreducible representation corresponding to the intermediate state at the top, and the final state at the left. Here the initial state is assumed to be totally symmetric. For the groups containing three-, four- or sixfold axes, it is convenient to take the RST in a circular coordinate system. We can derive the non-resonance case from Table II as well: to do this, we must add the tensors corresponding to different intermediate states, i.e., sum the tensors over the rows in Table II. As an example, let us examine the case in which the final state has the symmetry of the irreducible representation A_1 of the group C_{4v} . Summing over the row, we find that the RST for this final state has the form

$$\begin{bmatrix} 0 & a_2 & 0 \\ a_2 & 0 & 0 \\ 0 & 0 & a_1 \end{bmatrix}$$

Similarly we can examine the non-resonance case for a group of any crystal class. Using Table II, it is not hard to obtain the intensity table or find the degree of depolarization. Often one can experimentally determine the symmetry of a vibration manifested in the Raman spectrum even from the degree of depolarization.^[92-95] For more complex cases, we must also find the intensity table.

We note that a classification of the vibrations in certain ferroelectric crystals has been carried out (see^[96]) on the basis of experimental data, using Table II in particular. Apparently, the results of the experimental studies^[97-100] would also have been more definite if the intensity table had been found therein.

We also note that the structure of a number of crystals (based on comparing the spectra of the crystals with those of the same compounds in solution), the classification of vibrations, and other problems studied with the aid of Raman scattering in crystals have been discussed in some interesting papers by Mathieu and his associates.^[101-104]

We shall discuss here especially the case of

molecular crystals. The form of the Raman-scattering tensor for them is

$$a_{xy}^{(\mu)} = \sum_{\alpha g} a_{xy}^{(\alpha g)} u_{\alpha g, \mu}, \quad (9.1)$$

where $a_{xy}^{(\alpha g)}$ is the Raman-scattering tensor for an isolated molecule occurring at the site α in the unit cell, and the index g indicates the state of the isolated molecule. The index μ specifies the crystal vibrations, and the coefficients $u_{\alpha g, \mu}$ are defined in Sec. 2. Very often it proves possible to determine these coefficients even from purely group-theoretical considerations.^[105] Using Eq. (9.1), we can find the tensor $a_{xy}^{(\mu)}$ if we know the tensor $a_{xy}^{(\alpha g)}$. In many cases, we can find the latter by using Table II and the experimentally-determined degree of depolarization (for further details, see^[77]). Thus, if we know the symmetry of a vibration for the free molecule, the degree of depolarization measured for gases, and also the crystal structure, we can derive the intensity table. Insofar as we know, such a relatively easy program has not yet been carried out as applied to concrete crystals.

Using group theory, it proves possible to get definite information on the intensity table for Raman scattering in the harmonics and combination frequencies and to take into account the presence of Fermi resonance and effects involving temperature change (for further details, see^[106]).

We shall discuss these problems in more detail; first we shall take up the case of a harmonic. For this purpose, we shall determine the characters of the representation according to which the wave functions of the harmonic transform. We can find these characters either by the method of Tisza,^[107] or by that of Kompaneets.^[108] The existing representation of a harmonic can be either reducible or irreducible. If it is irreducible, then we can use Table II directly to find the form of the RST of the harmonic. However, if it is reducible, then the harmonic consists of a set of sublevels, and the form of the RST can be found separately for each sublevel using the same Table II. The intensities associated with each sublevel are added.

It is even easier to treat a combination frequency, since the corresponding representation is the direct product of the representations for the constituent levels, and there is no need to use any special method. Transition from the first excited vibrational level to the second becomes important with increasing temperature. By following the methods described above, we can easily find the set of tensors corresponding to this transition.

We can make the following remarks on how to take Fermi resonance into account in the Raman spectrum. As has been mentioned above, a harmonic in the general case splits into sublevels. Only those sublevels will participate in the resonance that trans-

Table II. (continued)

Group D_4					Group T			
	A_2	E				x	y	z
		ξ	η					
A_1	0 0 0	0 0 0	0 2 0	A	1 0 0	0 0 0	0 0 0	
	0 0 0	2 0 0	0 0 0		0 0 0	0 1 0	0 0 0	
	0 0 1	0 0 0	0 0 0		0 0 0	0 0 0	0 0 1	
A_2	0 0 0	0 0 0	0 -3 0	E	2 0 0	0 0 0	0 0 0	
	0 0 0	3 0 0	0 0 0		0 0 0	0 2 0	0 0 0	
	0 0 0	0 0 0	0 0 0		0 0 0	0 0 0	0 0 2	
E_2	0 0 0	0 0 0	4 0 0	F	3 0 0	0 0 0	0 0 0	
	0 0 0	0 0 0	0 0 0		x	0 0 0	0 3 0	0 0 0
	0 0 0	0 0 0	0 0 0			0 0 0	0 0 0	0 0 3
E_1	ξ	0 0 0	0 0 0	y		0 0 0	0 0 0	0 0 0
		0 0 0	0 4 0		0 0 0	0 0 0	0 0 4	0 0 0
		0 0 0	0 0 0		0 0 0	0 0 0	0 0 0	0 5 0
E_1	η	0 0 0	0 0 0	z	0 0 4	0 0 0	0 0 0	
		0 0 0	0 0 6		0 0 0	0 0 0	0 0 0	0 0 0
		0 5 0	0 0 0		0 0 0	0 0 0	0 0 0	5 0 0
		0 0 0	0 0 6		0 4 0	0 0 0	0 0 0	
		0 0 0	0 0 0		0 0 0	5 0 0	0 0 0	
		5 0 0	0 0 0		0 0 0	0 0 0	0 0 0	

form according to the same representation as the fundamental of the Fermi resonance. Hence, the resonance phenomenon will consist in the enhancement of specifically these selected sublevels.

In speaking of the application of group-theoretical methods to Raman scattering, we must not omit reference [109]. Here the so-called critical points of the vibrational spectrum were studied (the density of states is infinitely large at these points) using the topological methods developed in [110]. It was shown that they correspond to maxima of the scattering intensity. Hence the study of the shape of Raman lines permits one to study the relation of the vibration frequency to the wave vector in the neighborhood of critical points.

10. Raman scattering in piezoelectric crystals

This section will take up some peculiarities of Raman scattering by dipole vibrations that are also active in the infrared spectrum. As we have said (see Sec. 8), vibrations of this type occur only in piezoelectric crystals.

First we shall discuss these vibrations in cubic crystals, and shall assume for simplicity that the crystal is made of isotropic molecules. Among all the vibrations of the molecule, the only ones possessing a dipole moment are the triply degenerate vibrations transforming like x , y , and z . In the crystal the threefold degeneracy is partially removed. A non-degenerate longitudinal vibration and a doubly-degenerate transverse vibration are formed.* The longitudinal vibration induces a longitudinal electric field;

the existence of this field causes the frequency of the longitudinal vibration to be greater than that of the transverse vibrations, for which there is no similar field.

We can find the values of these frequencies if we know the relation of the dielectric constant to the frequency $\epsilon(\omega)$. In particular, the frequency of the longitudinal vibration is determined by the condition $\epsilon(\omega_{||}) = 0$, while the frequency of the transverse vibration is determined by the condition $\epsilon(\omega_{\perp}) = \infty$. The size of the splitting $\Delta\omega = \omega_{||} - \omega_{\perp}$ here is independent of the direction of the wave vector of the vibration.

We shall proceed now to non-cubic crystals, and for concreteness we shall study a crystal of the tetragonal system with a primitive lattice (one molecule per unit cell) formed by molecules of symmetry D_4 . The dipole vibrations in the molecule comprise one type of non-degenerate vibrations, and one of doubly-degenerate vibrations. Let us examine how a non-degenerate vibration polarized along the fourfold axis will behave in the crystal. The longitudinal field accompanying this vibration can be written as $\mathbf{E}_{||} = -4\pi\mathbf{k}(\mathbf{k} \cdot \mathbf{p})$ (where \mathbf{k} is the wave vector and \mathbf{p} is the dipole moment per unit volume). The change in the elastic constant for this vibration and hence also the change in the square of the frequency are proportional to the projection of the field $\mathbf{E}_{||}$ on the direction of \mathbf{p} . Hence, the frequency of a non-degenerate vibration depends on the angle φ between \mathbf{k} and \mathbf{p} (or, equivalently, that between \mathbf{k} and the fourfold axis) according to the formula

$$\omega^2 = \omega_0^2 + \Delta \cos^2 \varphi, \tag{10.1}$$

where ω_0 and Δ are constants.

*Strictly speaking, we can refer to the vibrations as being transverse or longitudinal in this case only for long waves.

Now we shall discuss a vibration that is doubly degenerate in the isolated molecule. Let the plane of the vibration be the xy plane. In this plane, let us choose two perpendicular unit vectors τ and σ , such that the unit vector σ lies in the plane formed by the z axis and the vector k . Let us resolve the degenerate vibration into components along τ and σ . The vibration along τ , and hence orthogonal to k , is not subject to the action of the longitudinal field, while vibration along σ can be treated as a non-degenerate vibration. Hence, the frequency of a vibration polarized along σ can be determined by Eq. (10.1). However, here we must take ϕ to be the angle between τ and k .

We have limited ourselves above to a primitive lattice for simplicity. As has been shown in [77], the relation of the frequencies to the direction of k can also be described by Eq. (10.1) for an arbitrary crystal.

Consequently, the frequencies in a non-cubic crystal vary with the direction of k . That is, the vibration frequency is a non-analytic function of the wave vector when $k \rightarrow 0$. In fact, in a number of experimental studies, [112-115] a vibration frequency manifested in the Raman spectrum has been observed to vary as a function of the direction k , and satisfactory agreement was found with Eq. (10.1) (see also [116]).*

The degree of depolarization of the Raman scattering in piezoelectric crystals also shows a number of peculiarities, which were first explained by Poulet [117] as applied to cubic crystals. This explanation is semiphenomenological. It is graphic in nature, and is worth taking up in more detail.

In accord with the polarizability theory,† the Raman scattering intensity is determined by the derivative $\partial\alpha/\partial q$ (where α is the polarizability of the crystal, which depends on the displacements q_x , q_y , and q_z of the ions along the x , y , and z axes; q is the generalized coordinate corresponding to the vibration manifested in the Raman spectrum).

Consequently, the intensity of the Raman scattering by a longitudinal vibration is determined by the derivative

$$\frac{\partial\alpha}{\partial q_{\parallel}} = \frac{\partial\alpha}{\partial q_x} \frac{\partial q_x}{\partial q_{\parallel}} + \frac{\partial\alpha}{\partial q_y} \frac{\partial q_y}{\partial q_{\parallel}} + \frac{\partial\alpha}{\partial q_z} \frac{\partial q_z}{\partial q_{\parallel}}. \quad (10.2)$$

The form of the tensors $\partial\alpha/\partial q_x$, $\partial\alpha/\partial q_y$, and $\partial\alpha/\partial q_z$ is known, and can be found in [89]. Then, using (10.2) we can obtain the form of the RST for the longitudinal vibration and find the intensity table

or the degree of depolarization, since $\partial q_x/\partial q_{\parallel} = k_x/|k|$, etc. We can treat analogously the scattering by the transverse vibrations; its intensity is determined by the formula

$$\frac{\partial\alpha}{\partial q_{\perp}} = \frac{\partial\alpha}{\partial q_x} \frac{\partial q_x}{\partial q_{\perp}} + \frac{\partial\alpha}{\partial q_y} \frac{\partial q_y}{\partial q_{\perp}} + \frac{\partial\alpha}{\partial q_z} \frac{\partial q_z}{\partial q_{\perp}}, \quad (10.3)$$

where q_{\perp} is one of the two transverse vibrational coordinates. Since the transverse vibrations are degenerate, the Raman scattering intensities from these vibrations must be added. The so-called "anomalies" in the degree of depolarization in piezoelectrics [119-120] were explained in [114] by directly using Eqs. (10.2) and (10.3).

We present Table III, which has been taken from [114]. It compares the theoretical and experimental data on the degree of depolarization for eight different cases of crystal orientation; here ρ_{\parallel} denotes the degree of depolarization for a longitudinal vibration, and ρ_{\perp} for a transverse vibration. The various cases differ from one another in the position of the detector, the orientation of the crystal, and the polarization direction (for further details, see the explanation for Table III). We see from the table that the degrees of depolarization calculated using Eqs. (10.2) and (10.3) and those observed experimentally agree satisfactorily.

We shall now make a special examination of the problem of the ratio of the scattering intensity from a longitudinal vibration to that from the transverse vibrations. If we assume that the coefficients $\partial\alpha/\partial q_x$, $\partial\alpha/\partial q_y$, and $\partial\alpha/\partial q_z$ are the same in (10.2) and (10.3), then the ratio of the cited intensities does not turn out equal to that actually observed experimentally. [116, 120] In order to eliminate this discrepancy, Poulet took different values for these coefficients in (10.2) and (10.3). It was later possible to determine the corresponding coefficient from independent experiments on the elasto-optic constants.

We note that the ideas presented in [117] were further developed in [121-124], which were concerned with studying Raman spectra in piezoelectric crystals (see also in this regard the review [125]). In connection with what has been said, we also note that one can show within the framework of the microtheory of Raman scattering presented above (see [126]) that the piezoelectric tensor (8.3) is not zero for longitudinal vibrations, while it vanishes for the transverse vibrations. This shows that it is essential to take into account the polarity of a vibration, and consequently, Poulet's procedure [117] for cubic crystals, is strictly substantiated. Thus the microtheory [126] has fully confirmed the validity of the phenomenological theory. [117] Besides, it has made it possible to find an explicit expression for the RST.

The treatment above was concerned with finding the form of the RST in cubic crystals. The behavior of non-cubic crystals has been discussed in [77, 127]. Here it was shown that the form of the RST for a

*Evidently the angle ϕ in (10.1) is $\pi/2$ for transverse vibrations.

†The application of the polarizability theory in crystals is subject to some doubt. Reference [118], which is concerned with substantiating the polarizability theory in crystals, does not take into account, e.g., the existence of the piezoelectric tensor (8.3), which plays a considerable role in this case.

Table III. Comparison of the theoretical and experimental data on depolarization

Case No.	Experiment		Theory		Case No.	Experiment		Theory	
	$\rho_{ }$	ρ_{\perp}	$\rho_{ }$	ρ_{\perp}		$\rho_{ }$	ρ_{\perp}	$\rho_{ }$	ρ_{\perp}
1	2.8	0.9	3	1	5	0.6	14	0.5	—
2	1.4	0.06	2	0	6	0.6	0.3	0.75	0.17
3	2.3	0.7	3	1	7	1.8	0.06	—	0
4	0.4	1.1	0.33	1	8	0.35	0	0.33	0

The X, Y, and Z axes are fixed (laboratory system); the radiation is incident on the crystal along the X axis, and the detector for the scattered radiation lies in the Y direction. The x, y, and z axes are the symmetry axes of the crystal, which is cut in the form of a cube having axes r, s, and t.

Case 1: the axes r, s, and t coincide with x, y, z and X, Y, Z, and the incident light is unpolarized. Case 2: the same, but the light is polarized along the Y axis. Case 3: the r, s, t trihedron is rotated by 45° about the z axis, the axis of it is parallel to OX, and the incident light is unpolarized. Case 4: the same, but without of parallel to OY. Case 5: the same as Case 4, but with the light polarized along E_y. Case 6: the axis of coincides with a threefold axis, the axis ox is perpendicular to ot and lies in the toz plane, os completes the trihedron, ot and OX are parallel, the angle toz is 54°44', the axis oz lies in the XOY plane, and the incident light is unpolarized. Case 7: the same, but with the incident light polarized along E_z. Case 8: the same as 7, but with k and z forming an angle of 99°44'.

non-degenerate vibration is given by the formula

$$a = a_z(1 + \epsilon \cos^2 \varphi), \tag{10.4}$$

where a_z is the form of the RST for a vibration polarized along z, ϵ is a constant, and φ is the angle between z and k.

For a vibration polarized along the previously-defined vector σ , the RST is given by the formula

$$a_{\sigma} = [a_x \cos(x, \sigma) + a_y \cos(y, \sigma)](1 + \epsilon \cos(\sigma, k)). \tag{10.5}$$

For a vibration polarized along τ , it is given by

$$a_{\tau} = a_x \cos(x, \tau) + a_y \cos(y, \tau). \tag{10.6}$$

Here we have introduced the notation: a_x, a_y are the RST for vibrations along the x and y axes, respectively.

The given formulas (10.4) and (10.5) imply that in general the RST depends on the direction of the wave vector of the vibration. This dependence results in an asymmetry of the Raman-scattering indicatrix. Insofar as we know, this has not yet been observed experimentally. In line with the theory presented above, this asymmetry must occur only for polar vibrations and be accompanied by a change in the vibration frequency manifested in the Raman scattering as the scattering angle is varied.

In speaking of the Raman-scattering indicatrix, we must mention some interesting peculiarities observed when Raman scattering is excited by a high-power light flux. However, this set of problems has already been taken up in sufficient detail in a review,^[84] and we shall not treat it here.

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